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**1913. Vol. CIII.**

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## 1914.

### *International Atomic Weights.*

| | | O=16. |
|---|---|---|
| Aluminium | Al | 27·1 |
| Antimony | Sb | 120·2 |
| Argon | A | 39·88 |
| Arsenic | As | 74·96 |
| Barium | Ba | 137·37 |
| Bismuth | Bi | 208·0 |
| Boron | B | 11·0 |
| Bromine | Br | 79·92 |
| Cadmium | Cd | 112·40 |
| Cæsium | Cs | 132·81 |
| Calcium | Ca | 40·07 |
| Carbon | C | 12·00 |
| Cerium | Ce | 140·25 |
| Chlorine | Cl | 35·46 |
| Chromium | Cr | 52·0 |
| Cobalt | Co | 58·97 |
| Columbium | Cb | 93·5 |
| Copper | Cu | 63·57 |
| Dysprosium | Dy | 162·5 |
| Erbium | Er | 167·7 |
| Europium | Eu | 152·0 |
| Fluorine | F | 19·0 |
| Gadolinium | Gd | 157·3 |
| Gallium | Ga | 69·9 |
| Germanium | Ge | 72·5 |
| Glucinum | Gl | 9·1 |
| Gold | Au | 197·2 |
| Helium | He | 3·99 |
| Holmium | Ho | 163·5 |
| Hydrogen | H | 1·008 |
| Indium | In | 114·8 |
| Iodine | I | 126·92 |
| Iridium | Ir | 193·1 |
| Iron | Fe | 55·84 |
| Krypton | Kr | 82·92 |
| Lanthanum | La | 139·0 |
| Lead | Pb | 207·10 |
| Lithium | Li | 6·94 |
| Lutecium | Lu | 174·0 |
| Magnesium | Mg | 24·32 |
| Manganese | Mn | 54·93 |
| Mercury | Hg | 200·6 |
| Molybdenum | Mo | 96·0 |
| Neodymium | Nd | 144·3 |
| Neon | Ne | 20·2 |
| Nickel | Ni | 58·68 |
| Niton (radium emanation) | Nt | 222·4 |
| Nitrogen | N | 14·01 |
| Osmium | Os | 190·9 |
| Oxygen | O | 16·00 |
| Palladium | Pd | 106·7 |
| Phosphorus | P | 31·04 |
| Platinum | Pt | 195·2 |
| Potassium | K | 39·10 |
| Praseodymium | Pr | 140·6 |
| Radium | Ra | 226·4 |
| Rhodium | Rh | 102·9 |
| Rubidium | Rb | 85·45 |
| Ruthenium | Ru | 101·7 |
| Samarium | Sa | 150·4 |
| Scandium | Sc | 44·1 |
| Selenium | Se | 79·2 |
| Silicon | Si | 28·3 |
| Silver | Ag | 107·88 |
| Sodium | Na | 23·00 |
| Strontium | Sr | 87·63 |
| Sulphur | S | 32·07 |
| Tantalum | Ta | 181·5 |
| Tellurium | Te | 127·5 |
| Terbium | Tb | 159·2 |
| Thallium | Tl | 204·0 |
| Thorium | Th | 232·4 |
| Thulium | Tm | 168·5 |
| Tin | Sn | 119·0 |
| Titanium | Ti | 48·1 |
| Tungsten | W | 184·0 |
| Uranium | U | 238·5 |
| Vanadium | V | 51·0 |
| Xenon | Xe | 130·2 |
| Ytterbium (Neoytterbium) | Yb | 172·0 |
| Yttrium | Yt | 89·0 |
| Zinc | Zn | 65·37 |
| Zirconium | Zr | 90·6 |

XVII.

JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

# I.—*Nitrites of the Alicylic Ammonium Series. Nitrosopiperazinium Nitrite.*

By Prafulla Chandra Rây and Jitendra Nath Rakshit.

In previous communications it has been shown that the alkylamines of the primary, secondary, and tertiary series invariably yield the corresponding nitrites. The investigation has now been extended to the members of the alicylic groups, and piperazine was selected as a typical representative.

Following the general method, piperazinium chloride solution was treated with silver nitrite, and the filtrate was evaporated in a vacuum over sulphuric acid, when glistening, pale yellow crystals were obtained. On submitting the solution to the usual Crum-Frankland and "urea" tests a curious anomalous behaviour was noticed. The ratio of the total nitrogen to the nitritic nitrogen was found to vary in different preparations; thus, in one instance it was 2·43, in another 2·60, whilst in the third it was 3·4. If the substance were a pure nitrite, this ratio should invariably have been unity. At first these fluctuations led us to conclude that the substance obtained was a mixture of nitrate and nitrite in varying proportions; but, on the other hand, a strong base like piperazine would be expected to yield a stable nitrite. In one preparation it was noticed that crystals began to separate out after an interval of two hours; these were collected and dried with filter paper, and were found to be very sparingly soluble in water. The solution on being shaken in the nitrometer with sulphuric acid gave nitric oxide, but on treatment with carbamide and dilute sulphuric acid no gas was liberated. Similarly, a solution of potassium iodide acidified with dilute sulphuric acid when placed in the nitrometer gave only a faint yellow tint, but no evolution of gas. The latter on being kept for some time began to deepen in colour owing to liberation of iodine, with evolution of nitric oxide, but the reaction was slow, and was only completed after an interval of several hours. It soon became evident that the first crop of crystals consisted, not of a nitrite at all, but simply of dinitrosopiperazine (m. p. 156°. Found, N = 19·47. Calc., N = 19·45 per cent.). The solution of this compound also proved to be practically a non-electrolyte; that it liberates iodine with evolution of nitric oxide on prolonged contact with the acidified solution of potassium iodide is, no doubt, due to its slowly undergoing hydrolysis. Peculiar interest, however, attaches to the fact that this dinitroso-compound gives up nitric oxide readily on being shaken with sulphuric acid in the nitrometer like an ordinary nitrate. A typical aliphatic nitroso-compound like nitrosodiethylamine does not, however, respond to this test. It thus became evident that the product obtained on evaporation to dryness in the earlier stages was a mixture of dinitrosopiperazine with the nitrite of the same base.

In view of the experiments described above, the following method was adopted for the isolation of pure nitrosopiperazinium nitrite. The solution obtained by double decomposition between piperazinium chloride and silver nitrite, which to start with gave the ratio of nitrogen by the Crum-Frankland and the "urea" method respectively as 2 : 1, was subjected to partial evaporation in a vacuum over sulphuric acid, and the successive crops which began to be deposited from day to day were separately collected. As a rule, the first two crops were found to be the pure dinitroso-compound—the third and fourth were more or less mixtures of the former with nitrosopiperazinium nitrite; at what particular stage the dinitroso-compound ceases to separate out depends on the concentration of the initial solution. If the concentration is hastened on the water-bath, dinitrosopiperazine is preferentially formed, and begins at once to crystallise out. Analyses of five distinct crops of as many preparations showed that the ratio nitrosic * to nitritic nitrogen was exactly unity. It might be urged that the substances that were obtained consisted of mixtures in well-nigh equivalent proportions of dinitrosopiperazine and piperazïnium dinitrite, but

---

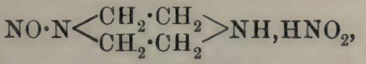
* As nitrosopiperazine yields nitric oxide just like an ordinary nitrate on treatment with sulphuric acid in a nitrometer, whilst the nitroso-group does not respond to the "urea" test, the differentiation made above thus seems to be justifiable.

this is out of the question, as the former is very sparingly soluble, whilst the latter is very readily soluble in water. One hundred parts of water at 30° dissolve only 0·45 part of nitrosopiperazine; it can therefore scarcely be expected that even in the sixth crop the two compounds should persist in separating out in equal proportions. A complete analysis of the sixth crop gave the following result:

0·1304 gave 0·1504 $CO_2$ and 0·0772 $H_2O$. $C=31\cdot39$; $H=6\cdot62$.
0·0580 „ 18·4 c.c. $N_2$ (moist) at 28·4° and 760 mm. $N=34\cdot67$.
$C_4H_9ON_3,HNO_2$ requires $C=29\cdot63$; $H=6\cdot17$; $N=34\cdot57$ per cent.

If an alcoholic solution of piperazinium chloride is shaken with silver nitrite and the filtrate evaporated in a vacuum over sulphuric acid, the formula of the salt obtained approaches that of piperazinium dinitrite; thus in one preparation the ratio of total nitrogen by the Crum-Frankland method to that yielded by the "urea" method was $1\cdot7/1\cdot6=1\cdot06$. The yield was, however, very poor, as piperazinium chloride is only sparingly soluble in alcohol.

*Nitrosopiperazinium nitrite,*



$$NO\cdot N{<}\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}{>}NH,HNO_2,$$

is obtained in soft, green crystals; it is very readily soluble in water. The conductivity measurement at 25° is as follows:

| Dilution. | Equivalent conductivity. | Ionisation per cent. |
|---|---|---|
| 51 | 85·1 | 88·8 |
| 153 | 90·2 | 94·2 |
| 459 | 95·6 | 99·8 |

It will thus be seen that nitrosopiperazinium nitrite is ionised to the extent of about 89 per cent. at a dilution of 59 litres, and this might be expected from its behaviour as a nitrite of the ammonium type.

CHEMICAL DEPARTMENT,
PRESIDENCY COLLEGE, CALCUTTA.

## II.—*Chlorides of the Mercurialkyl- and Mercurialkylaryl-ammonium Series and their Constitution as based on Conductivity Measurements.*

By PRAFULLA CHANDRA RÂY and NILRATAN DHAR.

IN our previous investigation on the nitrites of the mercurialkyl- and mercurialkylaryl-ammonium series (T., 1912, **101**, 687) we have noticed a striking analogy between these and the corresponding chlorides as described by Pesci (*Zeitsch. anorg. Chem.*, 1897,

**15**, 225). It occurred to us that fresh light might be thrown on the vexed question of the constitution of the latter class of salts by a study of their conductivities, for which purpose they have been found to be sufficiently soluble in water. It will be shown below that our surmise has proved to be correct, and that the simplest formula is acceptable in every case, and that each and all of these compounds belong to the ammonium type of salts.

Pesci, for instance, describes mercuribenzylammonium chloride as a "triple salt" with the complicated formula:

$$C_7H_8NHgCl + C_7H_7{\cdot}NH_2,HCl + HgCl_2.$$

From the conductivity measurements it would appear that the simpler formula, $C_7H_7{\cdot}NH_2,HgCl_2$, is more appropriate, and that it yields the ions $(C_7H_7{\cdot}NH_2,HgCl)^{\cdot}$ and $Cl'$ in aqueous solution.

Franklin, on the other hand, has been led to propose a different system of nomenclature (*J. Amer. Chem. Soc.*, 1907, **29**, 35; 1912, **47**, 361). According to him, these compounds should be termed mercuric chloride with "amine, pyridine, and quinoline, etc., of crystallisation," or "ammonobasic mercuric chlorides."

## EXPERIMENTAL.

*Method of Preparation.*—The composition of this class of salts varies considerably according to the method of preparation adopted. Pesci (*loc. cit.*) and André (*Compt. rend.*, 1891, **112**, 995) and others have often used cold or boiling aqueous or alcoholic solutions of mercuric chloride or of the amines. We rigidly adhered to a uniform method, consisting in adding an aqueous solution of the amine to a concentrated solution of mercuric chloride with continuous stirring until the ammoniacal odour became persistent.

As the presence of the minutest trace of amine hydrochloride formed during the reaction would seriously interfere with the conductivity measurements, the precipitate was in each case very carefully and repeatedly washed by the aid of the pump, and finally dried, as a rule, in the steam-oven. It remains only to add that whereas mercuric nitrite invariably forms with amines, compounds of the "additive" type, mercuric chloride, on the other hand, yields, under similar conditions, compounds both of the "additive" and "substitutive" types; the latter tendency is very marked, probably owing to the fact that an atom of chlorine of mercuric chloride often combines with an atom of hydrogen of the amine to form hydrogen chloride. On account of wide divergence in their solubilities, no exact comparison is available, but a general idea may be easily obtained.

Since these compounds are sparingly soluble, and a minute quantity of impurity would seriously affect the accuracy of the results, very pure water is necessary; much precaution was therefore taken in purifying the water used for these conductivity measurements: its conductivity was $1{\cdot}1 \times 10^{-6}$ at 30°.

### *Mercuriammonium Chloride or Infusible White Precipitate,* $NH_2HgCl$.

The precaution necessary for the preparation of this substance in a state of purity has already been given in detail (*Zeitsch. anorg. Chem.*, 1902, **33**, 197). This compound has been included in the series, as it may be regarded as the parent substance from which the rest have been derived.

### *Mercurimethylammonium Chloride,* $NMe(HgCl)_2$.

This remarkable compound has not been described, as far as we are aware, by previous workers in this field. The equation of its formation, namely, $NHMe_2 + 2HgCl_2 = NMe(HgCl)_2 + 2HCl$, should incline one to regard it as methylamine in which two atoms of hydrogen have been replaced by the two HgCl radicles. Its constitution will be discussed in the proper place.

Found: Hg = 81·73; Cl = 13·95; C = 2·00.

$CH_3NCl_2Hg_2$ requires Hg = 80·00; Cl = 14·20; C = 2·40 per cent.

It is worthy of note that under the ordinary conditions we have not succeeded in preparing ethyl and propyl substituted compounds of the present series.

Pesci, it is true, has described the ethyl derivative, NHEtHgCl; but our attempts to prepare it ended in failure. The compound which was obtained by treating mercuric chloride with ethylamine gave Hg = 84·19, whilst NHEtHgCl requires Hg = 71·52 per cent. Propylamine yielded a dirty reddish-brown compound, which gave Hg = 84·88 per cent.

It is evident that in both these cases highly basic (oxy) salts were obtained, which enormously raised the percentage of mercury.

*Mercuriisobutylammonium chloride,* $NH(C_4H_9)HgCl$.

Found: Hg = 66·61. $C_4H_{10}NClHg$ requires Hg = 65·15 per cent.

*Mercuripiperazinium chloride,* $C_4H_9N_2{\cdot}HgCl$.

Found: Hg = 62·38. $C_4H_9N_2ClHg$ requires Hg = 62·30 per cent.

*Mercuribenzylammonium chloride,* $C_6H_5{\cdot}CH_2{\cdot}NH_2,HgCl_2$.

Found: Hg = 54·64. $C_7H_9NCl_2Hg$ requires Hg = 53·05 per cent.

*Mercuribenzylmethylammonium chloride,*

$C_6H_5{\cdot}CH_2{\cdot}NHMe,HgCl_2$.

Found: Hg = 51·75; Cl = 18·41. $C_8H_{11}NCl_2Hg$ requires Hg = 51·02; Cl = 18·11 per cent.

*Mercuribenzylethylammonium chloride*, $C_6H_5 \cdot CH_2 \cdot NHEt,HgCl_2$.

Found: Hg = 49·76. $C_9H_{13}NCl_2Hg$ requires Hg = 49·26 per cent.

*Mercuriethylenediammonium chloride*, $C_2H_4(NH)_2,2HgCl_2$.

Found: Hg = 67·25; Cl = 23·56. $C_2H_6N_2Cl_4Hg_2$ requires Hg = 66·44; Cl = 23·58 per cent.

*Mercuripyridinium chloride*, $C_5H_5N,1\frac{1}{2}HgCl_2$.

Found: Hg = 61·06. Theory requires Hg = 61·89 per cent.

*Mercuripicolinium chloride*, $C_5H_4MeN,HgCl_2$.

Found: Hg = 54·61. $C_6H_7NCl_2Hg$ requires Hg = 54·94 per cent.

*Mercurinicotinium chloride*, $C_{10}H_{14}N_2,1\frac{1}{2}HgCl_2$.

Found: Hg = 50·88; Cl = 19·95. Theory requires Hg = 52·77; Cl = 18·73 per cent.

*Mercuripiperidinium chloride*, $C_5H_{11}N,2HgCl_2$.

Found: Hg = 65·30; Cl = 21·93. $C_5H_{11}NCl_4Hg_2$ requires Hg = 63·79; Cl = 22·4 per cent.

*Mercurihexamethylenetetrammonium chloride*,

$(CH_2)_6N_4,2HgCl_2$.

Found: Hg = 57·94. $C_6H_{12}N_4Cl_4Hg_2$ requires Hg = 58·65 per cent.

The piperidine compound is of a deep yellow colour, and is obtained by adding an aqueous solution of piperidine to mercuric chloride solution, and then diluting with water. The other members of this group are either colourless or pale yellow.

### *Mercuriammonium Chloride (Infusible White Precipitate)*,
### $NH_2HgCl$.

| Dilution. | Molecular conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 950·2 | 420·48 | 425·1 | 210·24 |
| 1900·4 | 460·64 | 950·2 | 230·32 |
| 3800·8 | 480·68 | 1900·4 | 240·34 |
| 7601·6 | 498·34 | 3800·8 | 249·17 |

### *Mercurimethylammonium Chloride*, $CH_3N(HgCl)_2$.

| | | | |
|---|---|---|---|
| 3380 | 323·58 | 845 | 80·89 |
| 6760 | 367·93 | 1690 | 91·97 |
| 13520 | 395·32 | 3380 | 98·83 |
| 27040 | 416·58 | 6760 | 104·13 |

### *Mercuripiperidinium Chloride*, $C_5H_{11}N,2HgCl_2$.

| | | | |
|---|---|---|---|
| 2090 | 262·92 | 522·5 | 65·72 |
| 4180 | 275·35 | 1045·0 | 68·83 |
| 8360 | 285·32 | 2090·0 | 71·33 |
| 16720 | 313·50 | 4180·0 | 78·37 |

### *Mercuriethylenediammonium Chloride*, $C_2H_4(NH_2)_2,2HgCl_2$.

| Dilution. | Molecular conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 1000 | 207·35 | 250 | 51·84 |
| 2000 | 222·32 | 500 | 55·58 |
| 4000 | 235·35 | 1000 | 58·84 |
| 8000 | 240·58 | 2000 | 60·14 |
| 16000 | 251·52 | 4000 | 62·83 |

### *Mercurihexamethylenetetrammonium Chloride*, $(CH_2)_6N_4,2HgCl_2$.

| | | | |
|---|---|---|---|
| 578 | 109·32 | 144·5 | 27·33 |
| 1156 | 132·73 | 289·0 | 33·18 |
| 2312 | 145·42 | 578·0 | 36·47 |
| 4624 | 150·35 | 1156·0 | 37·59 |
| 9248 | 155·38 | 2312·0 | 38·84 |

### *Mercuribenzylethylammonium Chloride*, $C_7H_7\cdot NHEt,HgCl_2$.

| | | | |
|---|---|---|---|
| 3700 | 284·48 | 1850 | 142·24 |
| 7400 | 286·32 | 3700 | 143·16 |
| 14800 | 290·35 | 7400 | 145·17 |
| 29600 | 310·36 | 14800 | 155·18 |

### *Mercuribenzylmethylammonium Chloride*, $C_7H_7\cdot NHMe,HgCl_2$.

| | | | |
|---|---|---|---|
| 2735 | 260·47 | 1367·5 | 130·23 |
| 5470 | 273·58 | 2735·0 | 136·79 |
| 10940 | 275·18 | 5470·0 | 137·59 |
| 21880 | 280·42 | 10940·0 | 140·21 |

### *Mercuribenzylammonium Chloride*, $C_7H_7\cdot NH_2,HgCl_2$.

| | | | |
|---|---|---|---|
| 1080 | * 190·20 | 540 | 95·10 |
| 2160 | 216·00 | 1080 | 108·00 |
| 4320 | 230·32 | 2160 | 115·16 |
| 8640 | 235·64 | 4320 | 117·82 |
| 17280 | 248·56 | 8640 | 124·28 |

### *Mercuriisobutylammonium Chloride*, $C_4H_9\cdot NH\cdot HgCl$.

| | | | |
|---|---|---|---|
| 3075·0 | 95·32 | 1537·5 | 47·66 |
| 4612·5 | 98·58 | 2306·2 | 49·29 |
| 9225·0 | 109·53 | 4612·5 | 54·76 |
| 18450·0 | 120·35 | 9225·0 | 60·17 |

### *Mercuripiperazinium Chloride*, $C_4H_9N_2HgCl$.

| | | | |
|---|---|---|---|
| 1131 | 125·66 | 565·5 | 62·83 |
| 2262 | 130·32 | 1131·0 | 65·16 |
| 4524 | 133·56 | 2262·0 | 66·78 |
| 9048 | 137·38 | 4524·0 | 68·69 |
| 11896 | 139·98 | 9048·0 | 69·99 |

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* The value of the molecular conductivity depends on the velocity of the ions so that it is to be expected that its value would be different in different compounds. There is thus partial deviation from Werner's numbers.

*Mercuripicolinium Chloride*, $C_5H_4NMe,HgCl_2$.

| Dilution. | Molecular conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 7280 | 1137·50 | 3640 | 568·75 |
| 14560 | 1150·35 | 7280 | 575·17 |
| 29120 | 1205·85 | 14560 | 602·92 |

*Mercuripyridinium Chloride*, $2C_5H_5N,3HgCl_2$.

| | | | |
|---|---|---|---|
| 18206 | 1887·53 | 3034·4 | 314·59 |
| 36412 | 1892·33 | 6068·8 | 315·39 |
| 72824 | 1900·38 | 12137·6 | 318·39 |

*Mercurinicotinium Chloride*, $2C_{10}H_{14}N_2,3HgCl_2$.

| | | | |
|---|---|---|---|
| 2520 | 420·00 | 420 | 70·00 |
| 5040 | 460·32 | 840 | 75·87 |
| 10080 | 520·36 | 1680 | 86·72 |
| 20160 | 560·56 | 3360 | 93·42 |

This compound evidently gives three chloridions ($Cl'$) and a complex tervalent ion containing mercury.

### *Discussion of Results.*

From the foregoing table it is evident that the molecular conductivities of some of the salts are about 100 at a dilution of 1000, whilst others have a value of about 250 at the same dilution, except infusible white precipitate, which is probably decomposed into simpler parts, namely, $NHg_2Cl$ and $NH_4Cl$ (compare *Zeitsch. anorg. Chem.*, 1902, **33**, 205).

Adding to Werner's rule (Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, **12**, 35; 1894, **14**, 506), it is probable that the former class of compounds yields two univalent ions in solution, whilst the latter, with an average of 250 as their molecular conductivity, yield three ions; the nicotine compound yields four ions, the value of its molecular conductivity being 450 at the same dilution. Mercurimethylammonium chloride appears to be of special interest. The two radicles, HgCl, are symmetrically disposed. It would, therefore, be reasonable to expect that the two chloridions ($Cl'$) would behave similarly. The conductivity measurements actually bear this out. In solution the salt gives two chloridions ($Cl'$) and one complex bivalent positive ion containing mercury. The result obtained in this case confirms Werner's rule. Although this compound was provisionally regarded as methylamine in which two atoms of hydrogen have been replaced by the radicle HgCl, in reality it is an ammonium derivative.

The pyridine and nicotine compounds are so very sparingly soluble that no definite trustworthy conclusions can be drawn from their conductivity measurements.

In all these compounds mercury forms a part of a complex ion, so the ordinary tests for dimercurion ($Hg^{\cdot\cdot}$) fail (for example, precipitation with hydroxidion ($OH'$) or carbanion ($CO_3''$).

Previous workers have designated these as additive compounds, but most probably they are not of this nature, as is evident from the considerations which have been already applied in the case of the corresponding nitrites (*loc. cit.*), namely:

(1) Ordinary tests for dimercurion ($Hg^{\cdot\cdot}$) fail, so mercuric chloride cannot exist as such.

(2) The sum of molecular conductivities of the separate constituents is generally very much less than the actual conductivity of the salt (especially in the cases of piperazine, ethylenediamine, and benzylamine compounds).

(3) Tests for hydroxidion ($OH'$) would be obtained if the amines are in the free state, as they yield hydroxidion in water; but the solutions give no such test. Moreover, the constituents (mercuric chlorides and amines) are easily soluble in water, whilst the salts formed from them are practically insoluble.

From the above arguments it is almost certain that these compounds are not of an additive nature, but are typical complex salts. In the case of the most soluble ones (for example, hexamethylenetetramine and pyridine compounds), silver chloride is precipitated when argentión ($Ag^{\cdot}$) is introduced into the solution; thus, chloridion ($Cl'$) exists in the free state. So, in those compounds which yield only two ions the negative one is chloridion ($Cl'$), whilst the positive ion is a complex radicle containing mercury; for example, in hexamethylenetetrammonium mercurichloride the two ions are $(CH_2)_6N_4Hg_2Cl_3^{\cdot}$ and $Cl'$ respectively.

By the introduction of argention ($Ag^{\cdot}$) silver chloride is deposited and equilibrium is disturbed, and the whole of the chlorine is precipitated.

Adópting Werner's idea in these compounds it is evident that some of the chlorine atoms are directly combined with mercury, and form a part of the complex ion (compare Jörgensen (*Zeitsch. anorg. Chem.*, 1897, **14**, 410). As in the other class of salts already studied (Rây, Dhar, and Dey), the direct linking is not quite as stable as those described by Werner (compare "New Ideas on Inorganic Chemistry," English Trans., pp. 39—43).

The mercurisulphine compounds studied by Hilditch and Smiles (T., 1907, **91**, 39) are also complex compounds.

Silver compounds with the halogens as part of the complex positive ion have also been studied by Hellwig (*Zeitsch. anorg.*

*Chem.*, 1900, **25**, 187). Mercuric chloride and mercuric nitrite are feebly ionised, even at high dilutions. It is always seen that those electrolytes which are feebly ionised can easily form complexes (for example, mercuric iodide, mercuric cyanide, etc.). Abegg, in his "Theory of Electrolytic Dissociation" (English Trans., p. 117), has given a list of complex mercury compounds.

There is thus a distinct tendency in the case of mercury to form complex compounds.

From these arguments it is evident that the ammoniacal mercuric chlorides are typical complex salts with a tervalent, bivalent, or univalent complex radicle, containing mercury and the other part is always chloridion (Cl′).

Thus, these bivalent salts behave like a simple chloride, such as barium chloride or zinc chloride, whilst the univalent salts are quite similar to chlorides, such as ammonium chloride or sodium chloride.

It will be seen that the present investigation and the previous one on the corresponding nitrites mutually strengthen and confirm each other.

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## III.—*Equivalent Conductivity and Ionisation of Nitrites.*

By PRAFULLA CHANDRA RÂY and NILRATAN DHAR.

THE study of nitrites from the point of view of equivalent conductivity and ionisation was undertaken by Pick (*Diss.*, Breslau, 1906), but he worked only with a very limited number of salts. Ley and Kissel (*Ber.*, 1899, **32**, 1363) measured the equivalent conductivity of mercuric nitrite alone. Rây and Mukherjee (P., 1910, **26**, 173) studied the ionisation of a series of alkali nitrites from their cryoscopic behaviour. In our study of the nature of the complexes of potassium mercurinitrite we have incidentally measured the equivalent conductivities of mercuric nitrite, potassium nitrite, and potassium mercurinitrite (T., 1912, **101**, 965). With the view of throwing light on the constitution of this important group of salts, an exhaustive study of their equivalent conductivities and ionic behaviour has been undertaken. As a rule, crystals of these nitrites were prepared, and freed from adhering mother liquor. Generally, these salts were obtained by double decomposition between silver nitrite and the corresponding chloride and evaporation in a vacuum of the filtrate. Evaporation on the water-bath had to be avoided, as these nitrites undergo marked hydrolysis at high temperatures. The nitrites of the alkylammonium bases which have been included in this paper are those recently described by Rây and Rakshit (T., 1911, **99**, 1470; 1912, **101**, 141, 216). Sometimes, also, salts in solution only were obtained by double decomposition between barium nitrite and equivalent proportion of the corresponding sulphate in a tall cylinder (compare Rây and Dhar, *loc. cit.*). This procedure was necessary for those nitrites the solutions of which decompose when their concentrations are increased (for example, copper and nickel nitrites). The temperature was 20° ± 0·1°.

The water used in these measurements was purified by continuous distillation with a tin condenser, first by means of acid permanganate, and then of alkaline permanganate; all the joints also were of tin. This arrangement was that of Jones and Mackay (*Zeitsch. physikal. Chem.*, 1894, **14**, 317) with a few alterations. The conductivity of the water used was $1 \times 10^{-6}$ at 20°.

In the following tables the value of the maximum equivalent conductivity is obtained by adding the separate ionic mobilities of the cation and anion, since the maximum equivalent conductivity cannot be exactly obtained by ordinary measurements, the values being sometimes highly affected by hydrolysis.

The values of ionic mobility for the univalent ions at 18° are primarily based on Kohlrausch's figures. The small changes are due to the use of 0·496, instead of 0·497, for the cation transference number of potassium chloride and to the change of atomic weight adopted in 1911. The corrections for temperature were made by Kohlrausch's equation:

$$(\Delta K_{1^\circ}) = \frac{1}{K_{18^\circ}} \times \frac{K_2 - K_1}{t_2 - t_1}.$$

where $K_2$ and $K_1$ are the conductivities at the temperatures $t_2$, $t_1$; $\Delta K_{1^\circ}$ is the temperature-coefficient which gives the change of conductivity expressed as a function of conductivity, $K_{18}$, at 18° for a change in the temperature of 1°.

Also the following equation of Kohlrausch can be very advantageously used in obtaining the migration velocity of an ion at temperatures not far removed from 18°:

$$U_t = U_{18^\circ} \times \{1 + \alpha(t^\circ - 18^\circ) + \beta(t^\circ - 18^\circ)^2\}.$$

The values for $\alpha$ and $\beta$ are taken from Kohlrausch's tables (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1031).

The ionic mobility of nitrosion ($NO_2'$) at 25° = 61·7 (Vogel, *Zeitsch. anorg. Chem.*, 1903, **35**, 403), whilst Pick (*loc. cit.*) gives it as 63 at 25° and 57 at 18°. The latter values are probably a little too high, since he has taken the equivalent conductivity of silver nitrite at a molar concentration of 0·0265 = 69·4, the value which is actually found. This value is, however, higher than the actual value owing to hydrolysis.

### *Ammonium Nitrite.*

Crystals of ammonium nitrite sublimed in a vacuum were used in this experiment (compare Rây, Dhar, and Dey., T., 1912, **101**, 1185).

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 20·7 | 96·72 | 186·3 | 107·69 |
| 62·1 | 104·54 | 558·9 | 110·92 |

The calculated value of $\lambda_\infty$ for ammonium nitrite at 20° is 126·3.

### *Lithium Nitrite.*

Crystals of this salt were used in this measurement.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 6 | 70·32 | 162 | 100·00 |
| 18 | 75·00 | 486 | 102·05 |
| 54 | 91·52 | | |

The calculated value of $\lambda_\infty$ for lithium nitrite at 20° is 93·7.

### *Sodium Nitrite.*

Crystals were used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 9 | 78·98 | 243 | 109·55 |
| 27 | 94·40 | 729 | 119·50 |
| 81 | 103·05 | | |

The calculated value of $\lambda_\infty$ for sodium nitrite at 20° is 104·3.

### *Calcium Nitrite.*

Crystals of this salt were used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 5·8 | 79·99 | 156·6 | 108·75 |
| 17·4 | 96·66 | 469·8 | 130·26 |
| 52·2 | 103·57 | | |

The calculated value of $\lambda_\infty$ for calcium nitrite at 20° is 112·9.

### *Strontium Nitrite.*

Crystals were used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 12 | 85·55 | 324 | 120·00 |
| 36 | 92·30 | 972 | 124·91 |
| 108 | 111·11 | | |

The calculated value of $\lambda_\infty$ for strontium nitrite at 20° is 113.

### *Barium Nitrite.*

Crystals were used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 6·31 | 78·88 | 170·37 | 122·38 |
| 18·93 | 97·56 | 511·11 | 124·12 |
| 56·79 | 111·61 | | |

The calculated value of $\lambda_\infty$ for barium nitrite at 20° is 116·75.

Disturbances due to hydrolysis are very marked in this case.

### *Magnesium Nitrite.*

The conductivity experiment was made with solution.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 15·5 | 91·15 | 139·5 | 120·55 |
| 46·5 | 108·65 | 418·5 | 127·15 |

The calculated value of $\lambda_\infty$ for magnesium nitrite at 20° is 106·9.

### *Zinc Nitrite (in Solution).*

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 12·4 | 59·27 | 334·8 | 116·25 |
| 37·2 | 80·87 | 1004·4 | 117·65 |
| 111·6 | 104·30 | | |

The calculated value of $\lambda_\infty$ for zinc nitrite at 20° is 108·1.

This solution is very feebly acid. This is due to the hydrolysis of the salt.

### *Silver Nitrite.*

Crystals (purified by recrystallisation) were used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 70·6 | 70·32 | 635·4 | 110·32 |
| 211·8 | 85·73 | | |

The calculated value of $\lambda_\infty$ for silver nitrite at 20° is 115·2.

### *Tetramethylammonium Nitrite.*

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 20·4 | 83·52 | 163·2 | 103·83 |
| 40·8 | 95·51 | 326·4 | 106·53 |
| 81·6 | 101·12 | 652·8 | 109·65 |

The calculated value of $\lambda_\infty$ for tetramethylammonium nitrite at 20° is 99·2.

### *Phenyldimethylethylammonium Nitrite.*

Crystals were used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 25·6 | 79·11 | 691·2 | 93·24 |
| 76·8 | 82·82 | 2073·6 | 93·80 |
| 230·4 | 87·68 | 6220·8 | 94·20 |

The calculated value of $\lambda_\infty$ for phenyldimethylammonium nitrite at 20° is 85·4. This salt is feebly alkaline to litmus.

### iso*Butylammonium Nitrite.*

Crystals were used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 28 | 75·55 | 252 | 81·12 |
| 84 | 80·35 | 756 | 81·92 |

The calculated value of $\lambda_\infty$ for *iso*butylammonium nitrite at 20° is 91·3.

The solution is almost neutral to litmus.

### *Butylammonium Nitrite.*

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 16 | 65·91 | 128 | 75·23 |
| 32 | 66·99 | 256 | 84·10 |
| 64 | 67·85 | 512 | 89·50 |

The calculated value of $\lambda_\infty$ for butylammonium nitrite at 20° is 91·3.

The solution is feebly alkaline to litmus.

### *Allylammonium Nitrite.*

Viscous liquid was used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 17·8 | 79·46 | 160·2 | 96·50 |
| 53·4 | 87·12 | 480·6 | 102·25 |

The calculated value of $\lambda_\infty$ for allylammonium nitrite at 20° is 94.

The solution reacts feebly acid.

### *Dipropylammonium Nitrite.*

Crystals were used.

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 24 | 69·55 | 216 | 81·13 |
| 72 | 79·15 | 648 | 85·12 |

The calculated value of $\lambda_\infty$ for dipropylammonium nitrite at 20° is 82·9.

The solution reacts very feebly alkaline.

### *Propylammonium Nitrite.*

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 7·4 | 75·51 | 199·8 | 105·15 |
| 22·2 | 86·71 | 599·4 | 111·00 |
| 66·6 | 93·83 | | |

The calculated value of $\lambda_\infty$ for propylammonium nitrite at 20° is 95·4.

The solution reacts very feebly acid.

### *Tripropylammonium Nitrite.*

| Dilution. | Equivalent conductivity. | Dilution. | Equivalent conductivity. |
|---|---|---|---|
| 20·4 | 60·00 | 189·3 | 79·85 |
| 63·1 | 73·65 | 567·9 | 91·80 |

The calculated value of $\lambda_\infty$ for tripropylammonium nitrite at 20° is 78·2.

The solution is almost neutral to litmus.

### *Diethylammonium Nitrite.*

Crystals were used.

| Dilution. | Equivalent conductivity. |
|---|---|
| 23·3 | 81·55 |
| 69·9 | 90·25 |
| 209·7 | 95·53 |
| 629·1 | 100·32 |

The calculated value of $\lambda_\infty$ for diethylammonium nitrite at 20° is 88·7.

The solution reacts very feebly alkaline.

### *Triethylammonium Nitrite.*

| Dilution. | Equivalent conductivity. |
|---|---|
| 60 | 85·52 |
| 180 | 89·21 |
| 540 | 91·25 |

The calculated value of $\lambda_\infty$ for triethylammonium nitrite at 20° is 105·2.

The solution is almost neutral to litmus.

### *Nickel Nitrite (in Solution).*

| Dilution. | Equivalent conductivity. |
|---|---|
| 18·17 | 57·32 |
| 54·51 | 78·52 |
| 163·53 | 95·35 |
| 490·59 | 114·12 |

The calculated value of $\lambda_\infty$ for nickel nitrite at 20° is 94·0.

The solution is feebly acid to litmus.

### *Copper Nitrite (in Solution).*

| Dilution. | Equivalent conductivity. |
|---|---|
| 18·12 | 58·55 |
| 54·36 | 79·92 |
| 162·58 | 99·46 |
| 487·74 | 111·18 |

The calculated value of $\lambda_\infty$ for copper nitrite at 20° is 106·8.

The solution is feebly acid.

### *Sodium Mercurinitrite.*

(Rây, T., 1907, **91**, 2031.)

| Dilution. | Equivalent conductivity. |
|---|---|
| 100 | 229·35 |
| 300 | 250·00 |
| 900 | 266·72 |

Like its potassium analogue (*loc. cit.*), in concentrated solutions only this salt behaves as a complex salt with the ions $Na^{\cdot}$ and mercurinitrosion, $Hg(NO_2)_4''$; but as it is diluted it begins to decompose into its constituents, as is seen in the table; thus at a dilution of about 1000, the equivalent conductivity is nearly 265, showing that this salt behaves like a salt decomposing into three ions (compare Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, **12**, 35; 1894, **14**, 506). At higher dilutions the value of the equivalent conductivity increases very fast owing to decomposition.

The solution has a slightly acid reaction due to hydrolysis of mercuric nitrite, which more than counterbalances the alkalinity due to the hydrolysis of sodium nitrite.

### *Tetramethylammonium Mercurinitrite.*

Crystals were used.

| Dilution. | Equivalent conductivity at 30°. | Dilution. | Equivalent conductivity at 30°. |
|---|---|---|---|
| 76 | 101·60 | 684 | 129·31 |
| 228 | 115·72 | | |

Similarly, this salt behaves in a concentrated solution like a complex salt. On dilution it begins to decompose, and the equivalent conductivity attains the value of about 150 instead of nearly 100 at a dilution of 1000 (compare Werner and Miolati, *loc. cit.*). It shows slight acidity, due to the same reason as in the previous salt.

### *Mercurosomercuric Nitrite*, $2Hg(NO_2)_2,HgNO_2$ (*in solution*).

| Dilution. | Equivalent conductivity. |
|---|---|
| 187 | 62·33 |
| 561 | 80·10 |

The preparation of this salt* has been described by one of us (Rây, T., 1902, **81**, 645). It behaves like a univalent salt, giving only two ions in solution; thus the equivalent conductivity at a dilution of about 1000 litres is nearly 100. At very high dilutions the salt, like other complex salts, begins to dissociate into simpler parts.

In this salt the ions are mercurosion ($Hg^{\cdot}$) and the univalent complex ion dimercurinitrosion, $Hg_2(NO_2)_5'$. At very high dilutions the complex begins to decompose, and causes acidity due to the hydrolysis of mercuric nitrite which is formed.

---

* This salt exists only in solution; on evaporation it is converted into the nitrate.

### *Discussion of Results.*

The equivalent conductivities of the nitrites, as is evident from the foregoing tables, do not reach a maximum value since they undergo hydrolysis. In the alkali and alkaline earth nitrites, a weakly basic reaction is obtained, since the corresponding hydroxides are strong bases; whilst in the case of copper, zinc, nickel, mercury nitrites, etc., there is a feebly acid reaction since the hydroxides are very feeble bases, and this indirectly proves also that nitrous acid is not a very weak acid, thus corroborating the evidence of Schumann (*Ber.*, 1900, **33**, 1527) and Blanchard (*Zeitsch. physikal. Chem.*, 1902, **41**, 681).

In the case of the alkylammonium nitrites the behaviour would also depend on the strength of the amines (compare Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 191).

In the compounds studied by us, effects due to hydrolysis must be reckoned with, for on account of the high velocities of hydrion and hydroxidion, the value of $\lambda_\infty$ is seriously affected, even if the degree of hydrolysis is very small. The hydrolysis in the case of calcium nitrite is rendered evident from the milkiness of the solution when evaporated on a water-bath. In the case of strontium nitrite it is much more marked; in fact, a pellicle of strontium carbonate is formed on the surface, and the solution is found to be more and more alkaline. Pick also noticed the turbidity of calcium nitrite solution, but has overlooked the real cause of it (*loc. cit.*, p. 16). Hence the value of the equivalent conductivity of the nitrates as measured by Kohlrausch, Noyes, and Jacobsen is a little lower than the corresponding nitrites at a similar dilution, although the ionic mobility of nitranion is almost equal to that of nitrosion.

It is evident from this work that the amine nitrites behave like typical ionogens, and are similar to alkali and alkaline earth nitrites.

It will also be seen that the results arrived at by the conductivity measurements corroborate in the main those deduced from the cryoscopic method by Rây and Mukherjee.

We are now engaged in measuring the viscosity and the degree of hydrolysis of the nitrites, so that the true degree of dissociation of these salts may be ascertained.

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# IV.—*Viscosity and Association. Part III. The Existence of Racemic Compounds in the Liquid State.*

By Ferdinand Bernard Thole.

The question of the existence of liquid racemates is one that has received considerable attention during the past twenty years, and in few such problems have the experimental data and resulting deductions been more contradictory.

Such a result is somewhat to be expected, for the conclusions, in practically every case, have been based on the study of physical properties and constants, and few of these are sufficiently constitutive or accurate to give figures the interpretation of which is not open to doubt, especially as liquid racemates, if they do exist, are probably dissociated to a great extent into their components.

In two previous papers (T., 1908, **93**, 1815; 1910, **97**, 1249) the author attempted to solve the problem by determining the viscosities of active and inactive isomerides, since viscosity is undoubtedly one of the most valuable constitutive properties, and, moreover, is one which gives very accurate results with a limited quantity of material. The results showed that racemic compounds can exist in solution, although in most cases the racemate on solution dissociates either completely or to a very considerable extent into the mixture of dextro- and lævo-forms.

The following is a summary of the chief researches that have been published on this question:

*Colour.*—Byk has shown (*Zeitsch. physikal. Chem.*, 1904, **49**, 682) that solutions of copper tartrate and copper racemate differ in colour, the former being blue and the latter greenish-blue.

*Molecular Volume.*—Marchlewski found that tartaric acid in aqueous solution has a smaller specific volume than racemic acid, but Ranken and Taylor have pointed out (*Proc. Roy. Soc. Edin.*, 1907, **27**, 172) that these results, which agree with those of Perkin (T., 1887, **51**, 362), require confirmation.

*Molecular Weight.*—Anschütz and Raoult, who first determined the molecular weights of active and racemic dimethyl diacetyltartrates by the cryoscopic method, obtained no evidence of racemic complexes in solutions. Bruni and his co-workers (*Atti R. Accad. Lincei*, 1902, [v], **11**, 212; 1904, [v], **13**, 349) have more recently shown that whilst this result is true for dilute solutions, dissociation is only partial in more concentrated solutions in the cases of dimethyl racemate, dimethyl diacetylracemate, ammonium hydrogen racemate, and ethyl *dl*-dibromophenylpropionate.

*Affinity Constant.*—According to Ostwald (*Zeitsch. physikal. Chem.*, 1889, **3**, 372), active and inactive tartaric acids have the same conductivity.

*Temperature Effects.*—Pasteur and Ladenburg have shown that when certain dextro- and lævo-isomerides (*d*- and *l*-tartaric acids and *d*- and *l*-coniine) are mixed in the liquid condition heat is evolved, but Adriani (*Zeitsch. physikal. Chem.*, 1900, **33**, 453) does not accept this as evidence of racemate formation.

*Freezing-point Curves.*—A great deal of work has been done in this connexion on the lines laid down by Roozeboom (*Zeitsch. physikal. Chem.*, 1899, **28**, 494), the chief workers in this field being Adriani, who obtained curves consisting of two eutectics and one maximum at 50 per cent. in the cases of dimethyl tartrate, dimethyl diacetyltartrate, mandelic acid, and benzoyltetrahydroquinaldine, and Findlay and Hickmans (T., 1907, **91**, 905), who obtained similar curves with the *l*-menthyl mandelates. The latter authors have confirmed their conclusions by a series of solubility measurements (T., 1909, **96**, 1386). Kipping considers that racemic compounds may have a free existence in the liquid state, since *d*-hydrindamine *dl*-mandelate is resolvable by crystallisation from water, whilst *dl*-hydrindamine *d*-mandelate could not be so resolved (T., 1909, **95**, 405, 1386).

*Absorption Spectra.*—Stewart (T., 1907, **91**, 1537) determined the absorption spectra of aqueous solutions of dextro-, meso-, and racemic tartaric acids, and found that the absorption curve of the last-named acid began to diverge from that of the other forms at concentrations above 14 per cent.

*Viscosity.*—Ranken and Taylor have pointed out that in moderately concentrated solutions racemic acid has a lower viscosity than tartaric acid.

Beck (*Zeitsch. physikal. Chem.*, 1904, **48**, 670) has determined the viscosities of a number of active and inactive compounds in the fused state. In the cases of camphoroxime and carvoxime all methods agree that the inactive substance is a ψ-racemic mixture and not a true racemate. In the cases of dimethyl racemate and dimethyl diacetylracemate, freezing-point curves and cryoscopic measurements show the free existence of the racemic compound.

Beck states, however, that his viscosity results show no indication of a liquid racemate in any of the above-mentioned substances.

In two previous papers (T., 1908, **93**, 1815; 1910, **97**, 1249) the author investigated the viscosities of a number of active and inactive compounds in solution. In some cases the results must be taken with some reserve, owing to the difficulty of careful purification without inducing racemisation.

Definite evidence was, however, obtained that racemic acid can exist to a limited extent in aqueous solution, the dissociation being, however, nearly complete at low concentration. The dextro- and inactive octyl hydrogen phthalates in benzene solution possess identical viscosities, as do the mandelic acids in water and pyridine solutions. In the case of the mandelic acids in amyl acetate solution there appears to be a slight divergence of the viscosity-concentration curves for solutions of the active and inactive acids.

The differences are, however, very small, and, as was emphasised in the paper, the evidence afforded was merely suggestive, and not conclusive, of the existence of racemic mandelic acid in the solution.

From the above results the following conclusions may be fairly drawn:

(1) Although racemic compounds undoubtedly exist in many cases in the solid state, the evidence for their existence in solution or in the fused state is conflicting.

(2) The majority of the evidence seems to point to the limited existence of liquid racemate complexes, although dissociation takes place to a very considerable extent when a racemate passes into the liquid condition.

(3) In dilute solutions all the results show complete dissociation, and only in the case of more concentrated solutions is any evidence found of racemate existence; moreover, the degree of dissociation at a given concentration and the rate of dissociation with dilution depend on the nature of the solute and the solvent. In fact, the position appears precisely analogous to that of the electrolytic dissociation of salts in dilute solution, and is on a par with that of the existence of double salts in solution.

Through the kindness of Dr. Pickard and Mr. Kenyon a number of active and inactive alcohols have been placed at the author's disposal, and an opportunity has been thus afforded for extending considerably the previous viscosity determinations in connexion with this subject. At the same time, owing to very considerable improvements in the apparatus used, it has been possible to extend the measurements to a considerably wider range of substances.

## EXPERIMENTAL.

The manipulative difficulties involved in the determination of viscosities of the substances detailed below were considerably increased by the limited quantity of material and by the necessity for investigating in the fused state certain compounds which are solid at the ordinary temperature. It was necessary, therefore, to design a viscometer which should be capable of giving fairly accurate results with not more than 1 c.c. of liquid, and at the same time obviate the difficulty and waste of filtering fused solids into the apparatus (a precaution quite necessary with the older forms of viscometer).

The type of instrument used is figured below, and while based essentially on the Ostwald principle is provided with a horizontal capillary and with two small wells or sumps into which particles of foreign matter may settle.

The smaller instrument (Fig. 1) was used in the investigation of the active alcohols, and had a capacity of 0·7 c.c. The receiving limb was made of glass tubing of 3 cm. bore, and had a bulb of about 0·3 c.c. capacity near its lower end. The horizontal capillary was 5 cm. long and 0·03 cm. bore, and the measuring limb 20 cm. long and 0·2 cm. bore. The viscometer was suspended vertically in the thermostat, and filled with liquid until the meniscus registered with the etched lines *cd*, any excess being removed with a capillary pipette. Twenty minutes were allowed for complete drainage from the sides of the receiving limb, and the levels were then finally adjusted. The liquid was then drawn above the etched line *a*, and the time of flow of the upper meniscus from *a* to *b* noted, a lens being used to give increased accuracy in timing. The experimental results show that even on such a small scale consistent values can be obtained.

FIG. 1.

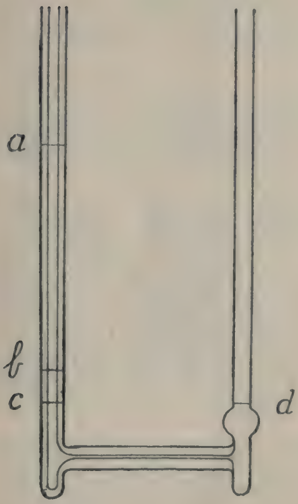
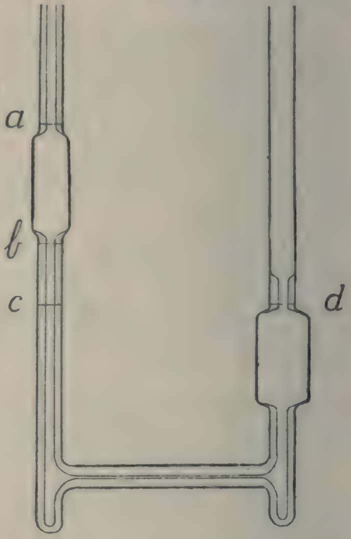


FIG. 2.



The average error is indicated by the following typical results with viscometers of the smaller type (0·7 c.c. capacity).

*Viscometer A.*—*l*-Heptan-β-ol.

| Time of flow in seconds. | |
|---|---|
| 213·4 | |
| 214·2 | Mean =214·0. |
| 214·4 | |
| 214·0 | |

| | | Viscosity. | Density. |
|---|---|---|---|
| Viscometer *A* | *l*-heptan-β-ol | 0·05055 | 0·8155 |
| ,, *C* | *d*-heptan-β-ol | 0·05042 | 0·8155 |
| ,, *A* | *d*-*n*-butyl*iso*propylcarbinol | 0·07088 | 0·8210 |
| ,, *C* | *d*- + *l*-butyl*iso*propylcarbinol | 0·07070 | 0·8212 |

In all the other cases sufficient material was available to permit the use of the larger apparatus (Fig. 2), which had a capacity of 2·4 c.c., and has now been adopted as the standard type of instrument in the present series of researches. For use with volatile or hygroscopic substances guard tubes of the type described in a previous paper (T., 1910, **97**, 2598) may be ground to the open ends of the limbs.

The viscometers were calibrated with ethylene dibromide, and in certain cases with aniline, liquids which are particularly suitable, as they can be readily obtained in a high state of purity.

The specific gravities at 25° were determined in Sprengel pyknometers, and at the higher temperatures in a small bulb of 3 c.c. capacity.

In the experiments at 25° the temperature of the bath was maintained within 0·01° by means of a Lowry spiral thermoregulator. For the higher temperatures a large beaker of water was used, the heating being controlled by hand, and the temperature maintained within 0·1°. Control of the temperature was greatly facilitated by covering the water with a film of mineral oil, which prevented rapid evaporation.

The octyl hydrogen phthalates were prepared from *sec.*-octyl alcohol by the method described by Pickard and Kenyon (T., 1907, **91**, 2058).

The menthyl mandelates were prepared from the acids and menthol by the Fischer-Speier methods described by McKenzie and Findlay and Hickmans respectively (T., 1904, **85**, 1254; 1907, **91**, 905).

The esters of tartaric and mandelic acids were purified by repeated fractional distillation under diminished pressure, care being taken to prevent the absorption of moisture by these substances (compare Beck, *Zeitsch. physikal. Chem.*, 1904, **48**, 670).

The *d*- and *l*-carvoximes were purified by crystallisation, and the inactive oxime was prepared by melting together equal weights of the isomerides.

The alcohols were lent by Dr. Pickard and Mr. Kenyon, and used without further purification.

### TABLE I.

*The Octyl Hydrogen Phthalates.*

| *Dextro.* | | *Inactive.* | |
|---|---|---|---|
| Temperature. | Time of flow (in seconds). | Temperature. | Time of flow (in seconds). |
| 65° | 151·6 | 65° | 153·9 |
| 71 | 113·6 | 70 | 120·1 |
| 76 | 90·2 | 75 | 94·0 |
| 80 | 77·4 | 80 | 77·5 |
| 85 | 63·5 | 85 | 63·4 |

Owing to lack of material, accurate density-determinations could not be made, and therefore times of flow were measured over a temperature range. The results when plotted are found to lie on a single curve, showing that no racemic compound is present.

This conclusion was previously arrived at from the viscosities of benzene solutions of these esters.

### TABLE II.

*The* ac-*Tetrahydronaphthols.*

| *Dextro.* | | *Inactive.* | |
|---|---|---|---|
| Temperature. | Time of flow (in seconds). | Temperature. | Time of flow (in seconds). |
| 34° | 231·3 | 31·1° | 296·4 |
| 40 | 141·7 | 38·0 | 165·0 |
| 48 | 81·7 | 44·0 | 106·0 |
| 55 | 54·0 | 50·0 | 71·6 |
| | | 55·0 | 53·4 |
| | | 62·4 | 36·7 |

In this case also the results lie on a single curve, showing the absence of any racemate in the inactive mixture.

### TABLE III.

*The Alcohols at* 25°.

| | Viscosity. | | | |
|---|---|---|---|---|
| Alcohol. | *d.* | *l.* | *dl* (found). | *dl* (calculated). |
| Phenylethylcarbinol ... | 0·1393 | 0·1306 | 0·1349 | 0·1344 |
| Heptan-β-ol ............ | 0·05042 | 0·05055 | 0·05055 | 0·05048 |
| Octan-β-ol ............... | 0·06328 | 0·06550 | 0·06490 | 0·06460 |

In the case of octan-β-ol the value in the third column is that of a mixture containing 60 per cent. of the dextro-form, and the viscosity value in column 4 is calculated for a mixture of this composition.

The results in the last two columns indicate clearly that the inactive mixture is only a conglomerate.

### Table IV.

*The Carvoximes.*

| *Fused at* 95°. | Viscosity. | *In amyl acetate solution at* 25° (1 *gram of oxime in* 7 *c.c. of solvent*) | Viscosity. |
|---|---|---|---|
| Dextro ......... | 0·0476 | Dextro ......... | 0·01109 |
| Inactive ......... | 0·0474 | Inactive ......... | 0·01111 |

Since the active forms of this oxime melt at 73° and the mixture at 92°, this might be expected at first sight to be a genuine case of the existence of a racemate. Adriani has, however, shown that the freezing-point curve exhibits a maximum at 50 per cent., but no eutectics. In other words, the substance melting at 92° consists of $\psi$-racemic mixed crystals, and is not a genuine racemic compound. This conclusion is amply confirmed by the viscosity results, both in the fused state and in solution. Beck has also determined the viscosities of various mixtures of *d*- and *l*-carvoximes, and his results are in full agreement with those detailed above.

### Table V.

*The Tartaric Esters.*

| Ester. | Temperature. | Viscosity. |
|---|---|---|
| Methyl *d*-tartrate ................... | 85° | 0·133 |
| ,, racemate ................... | 85 | 0·130 |
| ,, ,, + methyl tartrate (50 per cent.) ............ | 85 | 0·131 |
| Ethyl *d*-tartrate ................... | 25 | 1·457 |
| ,, racemate ................... | 25 | 1·360 |

The esters of tartaric acid (particularly the ethyl esters) are notably difficult to purify, especially in view of their hygroscopic nature.

In the cases investigated, therefore, repeated vacuum distillation was employed until approximately constant viscosity-values were obtained.

In the case of dimethyl racemate several methods, notably freezing-point curves and cryoscopic measurements, seem to indicate that this substance is capable of actual existence. The ester was investigated by Beck, who determined the viscosities of a range of mixtures of the dextro- and inactive esters. He concluded that his results were in sufficient agreement to preclude the possibility of the existence of a racemate. When plotted, however, they lie on by no means a smooth curve, and must be accepted with some reserve. The viscosities detailed above seem to indicate the probable existence to an appreciable extent of both dimethyl and diethyl racemates in the liquid state, the racemate, as in the case of the free acid, possessing a lower viscosity than the active form.

Beck further investigated the viscosities of fused dimethyl diacetyltartrate and dimethyl diacetylracemate, and concluded that the two esters had the same viscosity, showing the absence of any racemic compound. His results are appended, and it will be noticed that they are capable of another interpretation, since with one exception the viscosity falls with increasing concentration of the inactive ester.

### Table VI.

*Dimethyl Diacetyltartrate and Diacetylracemate at* 104° (Beck).

| Mixture. | Viscosity ($\eta$ of water at 25° = 1). |
|---|---|
| Pure racemate ........................ | 6·764 |
| 90 per cent. racemate ...............<br>10 ,, active ester ... ........ | 6·666 |
| 60 ,, racemate ........ .....<br>40 ,, active ester ............ | 6·912 |
| Pure active ester ...................... | 6·933 |

Bruni has proved by cryoscopic measurements that dimethyl diacetylracemate can exist in non-dissociating solvents, such as ethylene dibromide, and Adriani's freezing-point curve shows two eutectics and a maximum at 50 per cent. of each active form.

### Table VII.

*The* l-*Menthyl Mandelates.*

| | *Fused at* 85°. | *In amyl acetate solution at* 25° (1·1 *gram of ester in* 7 *c.c. of solvent*). |
|---|---|---|
| | Viscosity. | Viscosity. |
| *l*-Menthyl *dl*-mandelate ... | 0·0653 | 0·01110 |
| ,, *l*-mandelate ... | 0·0632 | 0·01085 |

These esters have been fully investigated by Findlay and Hickmans, who conclude from freezing-point curves and solubility determinations that the partly racemic ester is capable of free existence.

This conclusion is fully borne out by the above viscosity results.

### Table VIII.

*The Ethyl Mandelates at* 25°.

| Ester. | Viscosity. |
|---|---|
| Ethyl *dl*-mandelate ..................... | 0·1971 |
| ,, *l*-mandelate ........................ | 0·1971 |

These results demonstrate clearly that ethyl *dl*-mandelate is completely dissociated under the conditions of the determinations.

### *Summary of Results.*

(1) In most cases *dl*-liquids and solutions are merely conglomerates. This has been shown in the cases of octyl hydrogen phthalate, *ac*-tetrahydronaphthol, phenylethylcarbinol, heptan-β-ol, octan-β-ol, carvoxime, and ethyl mandelate.

In certain instances proof has been afforded by viscosity, and in some cases confirmed by other physical methods, of the existence in solution and in the fused state of racemic complexes.

The cases investigated in the present research were methyl and ethyl racemates and *l*-menthyl *r*-mandelate. It is perhaps worthy of mention that nearly all the definitely established liquid racemates are derivatives of the hydroxy-carboxylic acids.

(2) In the cases where racemate existence in solution has been substantiated, dissociation is very considerable, even at fairly high concentrations in a comparatively non-dissociating solvent.

The author desires to express his thanks to Dr. Pickard and Mr. Kenyon for the loan of material, and to the Research Fund Committee of the Chemical Society for a grant which has partly covered the expenses entailed.

East London College.

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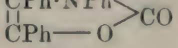
## V.—*The Formation of Tetrahydro-oxazoles from α-Hydroxy-β-anilino-αβ-diphenylethane and its Homologues.*

By Horace Leslie Crowther and Hamilton McCombie.

It has been shown by McCombie and Parkes (T., 1912, **101**, 1991) that α-keto-β-anilino-αβ-diphenylethane (I), when condensed with carbonyl chloride in toluene solution, yields 3 : 4 : 5-triphenyl-2 : 3-dihydro-2-oxazolone (II). It was found impossible, however, to convert this dihydro-oxazolone into a tetrahydro-oxazolone by the action of reducing agents, as the compound was either recovered unchanged or converted into dibenzyl, with complete destruction of the oxazole ring. In this respect the oxazole ring behaves very similarly to the glyoxaline ring, which it is found impossible to hydrogenise by the direct action of reducing agents:

$COPh{\cdot}CHPh{\cdot}NHPh$

(I.)



$\left.\begin{array}{l}\mathrm{CPh{\cdot}NPh}\\ \| \\ \mathrm{CPh{-\!-}O}\end{array}\right>\mathrm{CO}$

(II.)

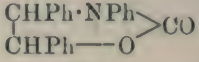
$CHPh(OH){\cdot}CHPh{\cdot}NHPh$

(III.)

Attempts have been made by the authors to obtain tetrahydro-oxazolones from $\alpha$-keto-$\beta$-anilino-$\alpha\beta$-diphenylethane by first reducing that compound to $\alpha$-hydroxy-$\beta$-anilino-$\alpha\beta$-diphenylethane (III), employing the method described by Voigt (*J. pr. Chem.*, 1886, [ii], **34**, 9), forming the ethylcarbonato-derivative (IV), and eliminating alcohol according to the method described by McCombie and Parkes (*loc. cit.*). This method, however, resulted merely in the regeneration of the original hydroxy-compound. A successful synthesis of tetrahydro-oxazolones was attained by the direct condensation of $\alpha$-hydroxy-$\beta$-anilino-$\alpha\beta$-diphenylethane (III) with carbonyl chloride in toluene solution, when there resulted 3:4:5-triphenyl-2:3:4:5-tetrahydro-2-oxazolone (V):

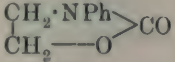
$CO_2Et{\cdot}O{\cdot}CHPh{\cdot}CHPh{\cdot}NHPh$

(IV.)



$\left.\begin{array}{l}\mathrm{CHPh{\cdot}NPh}\\ \mathrm{CHPh{-\!-}O}\end{array}\right>\mathrm{CO}$

(V.)



$\left.\begin{array}{l}\mathrm{CH_2{\cdot}NPh}\\ \mathrm{CH_2{-\!-}O}\end{array}\right>\mathrm{CO}$

(VI.)

By similar condensations the corresponding *m*- and *p*-tolyl and $\beta$-naphthyl derivatives were obtained, in which these substituents are attached to the nitrogen atom. It was found impossible to prepare the *o*-tolyl analogue because the conditions necessary for the reduction of $\alpha$-keto-$\beta$-*o*-toluidino-$\alpha\beta$-diphenylethane to the corresponding hydroxy-compound could not be discovered.

The tetrahydro-oxazolones described in this communication are closely related to 3-phenyl-2:3:4:5-tetrahydro-2-oxazolone (VI), which is described by Nemirowski (*J. pr. Chem.*, 1885, [ii], **31**, 175) and by Otto (*ibid.*, 1891, [ii], **44**, 17).

These tetrahydro-oxazolones were found to be very stable substances. They were not reduced by sodium amalgam, or even by sodium in amyl-alcoholic solution. Phosphorus trichloride was without action on them, and their basicity was so slight that no hydrochloride or picrate could be isolated.

It was thought possible that compounds similar to the sulphinazoles described by McCombie and Parkes (*loc. cit.*) might be prepared from these hydroxy-compounds by substituting thionyl chloride for carbonyl chloride in the reaction described above. In the case of the aniline compound a very small quantity of a condensation product was obtained. In the case of the other compounds, no trace of a condensation product could be isolated, so that evidently there is little or no tendency for thionyl chloride to yield cyclic compounds with these hydroxy-derivatives. Similar negative results were obtained when sulphuryl chloride was substituted for carbonyl chloride.

## EXPERIMENTAL.

### *α-Ethylcarbonato-β-anilino-αβ-diphenylethane*, $C_{23}H_{23}O_3N$.

This compound was obtained by dissolving the base in dimethylaniline and adding excess of ethyl chlorocarbonate. The mixture was allowed to remain in the cold for twelve hours, and was then poured into dilute hydrochloric acid. The carbethoxy-compound separated as a viscid mass, which, when recrystallised from dilute alcohol or light petroleum, melted at 114°:

0·2000 gave 7·2 c.c. $N_2$ at 14° and 739 mm. N=4·07.

$C_{23}H_{23}O_3N$ requires N=3·88 per cent.

This carbethoxy-compound, on treatment with alcoholic potassium hydroxide, gave α-hydroxy-β-anilino-αβ-diphenylethane.

### 3:4:5-*Triphenyl*-2:3:4:5-*tetrahydro-2-oxazolone*, $C_{21}H_{17}O_2N$.

This substance was obtained by dissolving 2 grams of α-hydroxy-β-anilino-αβ-diphenylethane in 25 c.c. of dry toluene, and adding 8 grams of carbonyl chloride in toluene (20 per cent. solution). The mixture was allowed to remain overnight, when a white product separated. The excess of carbonyl chloride was removed on the water-bath, and the solution was poured into light petroleum in order to precipitate the oxazole completely. The yield was nearly theoretical. The product, when crystallised from alcohol, separated in fine, white needles, which melted at 216°:

0·1781 gave 0·5200 $CO_2$ and 0·0914 $H_2O$. C=79·75; H=5·7.

0·1700 ,, 6·55 c.c. $N_2$ at 16° and 75·35 mm. N=4·44.

$C_{21}H_{17}O_2N$ requires C=80·00; H=5·4; N=4·45 per cent.

The tetrahydro-oxazolone is readily soluble in glacial acetic acid or acetone, fairly so in amyl alcohol or toluene, especially on heating, but quite insoluble in light petroleum.

The compound is very stable; attempts to reduce it with sodium amalgam, or even with sodium in amyl alcohol, yielded the unchanged substance, and phosphorus trichloride was found to be without action on it. No salts with hydrochloric acid or picric acid could be prepared

### *α-Hydroxy-β*-m-*toluidino-αβ-diphenylethane*, $C_{21}H_{21}ON$.

This compound was prepared from α-keto-β-*m*-toluidino-αβ-diphenylethane (McCombie and Parkes, *loc. cit.*, p. 1996) by reduction with sodium amalgam in exactly the same manner as that described later for the preparation of the β-naphthylamino-compound. It crystallised more easily than that compound from methylated spirit, separating in colourless needles which melt at 133°:

0·1825 gave 0·5544 $CO_2$ and 0·1180 $H_2O$. C=82·84; H=7·18.
$C_{21}H_{21}ON$ requires C=83·17; H=6·93 per cent.

### 4:5-*Diphenyl*-3-m-*tolyl*-2:3:4:5-*tetrahydro-2-oxazolone.*

This compound after recrystallisation from methylated spirit (in which is is only sparingly soluble), or from amyl alcohol, melted at 189°:

0·1808 gave 0·5329 $CO_2$ and 0·0906 $H_2O$. C=80·38; H=5·57.
$C_{24}H_{19}O_2N$ requires C=80·24; H=5·78 per cent.

### 4:5-*Diphenyl*-3-p-*tolyl*-2:3:4:5-*tetrahydro-2-oxazolone.*

When recrystallised from amyl alcohol or methylated spirit this substance melted at 209°:

0·1846 gave 0·5440 $CO_2$ and 0·0985 $H_2O$. C=80·37; H=5·93.
$C_{24}H_{19}O_2N$ requires C=80·24; H=5·78 per cent.

### *α-Hydroxy-β-2-naphthylamino-αβ-diphenylethane,*
### $OH{\cdot}CHPh{\cdot}CHPh{\cdot}NH{\cdot}C_{10}H_7$.

This substance was prepared from the corresponding keto-compound by reduction with sodium amalgam.

To 10 grams of α-keto-β-2-naphthylamino-αβ-diphenylethane dissolved in 100 c.c. of methylated spirit were added 50 grams of freshly prepared sodium amalgam (4 per cent.), and the mixture was kept almost at the boiling point for two to three hours. It was not found necessary to dissolve the compound completely in alcohol, for as the reduction proceeded, the compound was dissolved. The solution became dark in colour, and when reduction was complete, the solution was poured into boiling water, and allowed to remain for several hours before filtering. The separated solid was washed with dilute hydrochloric acid to remove any naphthylamine, and was then boiled with a small quantity of light petroleum until a white product was obtained. The mixture was cooled, the liquid was decanted from the white solid, and the latter was recrystallised from a larger bulk of light petroleum. Unless the impurities were removed by a preliminary extraction with light petroleum, recrystallisation was found to be impossible.

When pure, this substance is a white, crystalline solid, extremely soluble in all ordinary solvents, except light petroleum, from a large quantity of which it crystallises well and melts at 124—125°:

0·1831 gave 0·5694 $CO_2$ and 0·1011 $H_2O$. C = 84·81; H = 6·14.
$C_{24}H_{21}ON$ requires C = 84·95; H = 6·20 per cent.

### 4:5-*Diphenyl*-3-*β*-*naphthyl*-2:3:4:5-*tetrahydro*-2-*oxazolone*.

The recrystallised hydroxy-compound was dissolved in hot toluene, and, from time to time, small quantities of a 20 per cent. solution of carbonyl chloride in toluene were added, whilst the solution was kept hot on a sand-bath. After a time a white solid was precipitated, and when excess of carbonyl chloride had been added, the mixture was allowed to remain for some time. The excess of carbonyl chloride was removed by evaporation, and the solution, when cold, was poured into a large excess of light petroleum, which precipitated the oxazolone completely.

The substance when recrystallised from methylated spirit or amyl alcohol separated in large, white, silky needles, which melted at 231°. If the hydroxy-compound was pure, the yield of the oxazolone was nearly theoretical. The solubilities of the naphthyl derivative were very similar to those of the corresponding aniline compound:

0·1772 gave 0·5335 $CO_2$ and 0·0864 $H_2O$. C = 82·13; H = 5·42.
$C_{21}H_{19}O_2N$ requires C = 82·19; H = 5·21 per cent.

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# VI. *The Action of Halogens on Silver Salts.*

By HUGH STOTT TAYLOR (1851 Exhibition Scholar, University of Liverpool).

IN a recent communication it has been shown by Normand and Cumming (T., 1912, **101**, 1852) that the halogens react with silver salts to yield an insoluble silver haloid, an acid, and one or more oxidation products either of the acid or the haloid. In the simpler cases considered, namely, those in which no secondary oxidations occurred, interesting conclusions were drawn as to the variation in the products of reaction with the halogen used; thus (*loc. cit.*, p. 1855), it is pointed out that reactions with iodine usually result in the formation of an iodate. With chlorine and bromine the reactions yield, however, hypochlorous and hypobromous acids.

That iodine is quite analogous to the halogens chlorine and bromine in its action on alkali hydroxides has long been known. Schönbein (*J. pr. Chem.*, 1861, **84**, 385) established this in 1861, and his observations have since been extended and amplified (Berthelot, *Ann. Chim. Phys.*, 1878, [v], **13**, 20; Schwicker, *Zeitsch. physikal. Chem.*, 1895, **16**, 302; Foerster and Gyr, *Zeitsch. Elektrochem.*, 1903, **9**, 1; Skrabal, *Monatsh.*, 1907, **28**, 319; 1911, **32**, 167, 815). It would therefore be expected that in reactions with silver salts a similar analogy would be found to hold.

Thus, the interaction of iodine and an alkali yields hypoiodous acid according to the equation:

$$I_2 + OH' = HOI + I'.$$

With excess of alkali an equilibrium is set up:

$$HIO + OH' = IO' + H_2O.$$

Further, dissolved hypoiodites are unstable, and are converted in course of time into iodate according to the equation:

$$2HOI + IO' = IO_3' + 2HI.$$

With silver salts, therefore, owing to the insolubility of the silver iodide, the following equilibria would be expected:

$$AgX + I_2 + H_2O = AgI + HX + HIO \quad . \quad . \quad . \quad (1)$$

With excess of the silver salt the reaction should then proceed to the iodate stage in accordance with the equation:

$$3HIO + 3AgX = AgIO_3 + 2AgI + 3HX \quad . \quad . \quad . \quad (2)$$

The mechanism of reaction suggested by Birnbaum (*Annalen*, 1869, **152**, 111) and by Normand and Cumming (*loc. cit.*, pp. 1853, 1854) represents, according to such views, the sum of the two reactions (1) and (2).

As is evident from a study of the action of iodine on alkali hydroxides, the alkali hypoiodites are much less stable than the corresponding salts of chlorine and bromine, conversion to iodate occurring with a much greater velocity than is the case in the formation of chlorate or bromate. The velocity of conversion, also, is accelerated by rise of temperature and increase of concentration. It is probable, therefore, that with silver salts also the initial formation of hypoiodite will be the more easily demonstrable the lower the temperature of experiment and the smaller the concentration of the solutions employed. The validity of these assumptions was tested with iodine and silver nitrate in the following experiments, which were carried out some months previous to the appearance of the paper by Normand and Cumming. The analogous experiments with silver acetate have been performed subsequent to the publication of the work in question.

R. L. Taylor (*Mem. Manchester Phil. Soc.*, 1897, [viii], **41**, 1) in a paper on hypoiodous acid and hypoiodites first demonstrated that silver nitrate reacts with aqueous iodine solutions, the resulting solution giving all the reactions for hypoiodite. By titrating the solutions obtained with a standard solution of indigo-carmine, the author showed that the bleaching action immediately after the addition of silver nitrate corresponded with the formation of 95 per cent. of the hypoiodite demanded by theory. Further, it was shown that the solution so obtained was extremely unstable, and that after five minutes it had lost 90 per cent. of its bleaching power.

## EXPERIMENTAL.

### *Method of Estimation of Hypoiodite.*

It was noticed by R. L. Taylor that considerable uncertainty attaches to titration with indigo-carmine. With iodine-water an excess of indigo may be added and apparently bleached, but on keeping the blue colour returns. Similar difficulties were observed in the initial stages of the present investigation. Consequently, the method was rejected in favour of Schwicker's method (*Zeitsch. physikal. Chem.*, 1895, **16**, 303). By the addition to a hypoiodite solution of excess of a solution of sodium hydrogen carbonate saturated with carbon dioxide and also a solution of an iodide, it was shown by Schwicker that iodine is liberated equal in amount to twice the amount of iodine present as hypoiodite. The iodine liberated can then be titrated with sodium arsenite solution.

*Silver Nitrate and Iodine.*—An aqueous solution of iodine when treated with a solution of silver nitrate yields a pale yellow liquid containing silver iodide in a finely divided condition. If the volumes of the solutions are so chosen that equimolecular quantities of the two substances react, the solution obtained, when tested immediately for hypoiodite by the method of Schwicker, gives a titre corresponding on an average with the formation of 96 per cent. of the amount of hypoiodite required according to the equation:

$$AgNO_3 + I_2 + H_2O = AgI + HIO + HNO_3.$$

If the amounts taken are in the ratio of one atom of iodine to one molecule of silver nitrate, immediate titration for hypoiodite demonstrates the presence of about 90 per cent. of the total hypoiodite required by theory.

The low values obtained are due to the rapid decomposition of the hypoiodite into iodide and iodate according to the equation:

$$2HIO + IO' = IO_3 + 2HI.$$

The hydriodic acid formed is removed as insoluble silver iodide.

The decomposition is the more rapid the greater the concentration of silver salt present, as is evident from the following time reactions effected with solutions containing approximately 1, 2, and 3 molecules of silver nitrate respectively for each molecule of iodine. The method of procedure adopted in these experiments was to take a given volume of solution containing the materials in the required proportions, and then to titrate aliquot portions thereof at definite intervals of time. The first column indicates the time in minutes intervening between mixing and titration, the remaining columns the percentage of hypoiodite present.

| | Percentage hypoiodite with 1 molecule iodine and | | |
|---|---|---|---|
| Time. | 1 mol. $AgNO_3$. | 2 mols. $AgNO_3$. | 3 mols. $AgNO_3$. |
| 1 | 92·5 | 72·8 | 35·5 |
| 3 | 81·8 | 53·6 | — |
| 6 | 76·2 | 38·0 | 10·5 |
| 11 | 71·0 | 24·0 | 6·9 |
| 16 | 68·7 | — | 4·5 |
| 21 | 67·3 | 14·2 | 3·3 |
| 28 | — | 10·5 | — |
| 80 | 64·5 | — | — |

In the first example in which the materials are present in approximately equimolecular quantities, the hypoiodous acid is slowly converted into hydriodic acid and iodic acid. In its initial stages the conversion is assisted by the slight excess of silver salt necessary for the attainment of the first reaction, but after a period of time, during which the silver is removed as insoluble silver iodide, the rate of decomposition sensibly diminishes. Further, it is known that a mixture of hydriodic and iodic acids decomposes to yield iodine:

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

Regeneration of iodine would therefore be expected in the progress of the above reaction. That this occurs can be demonstrated by treating a mixture of molecular quantities of iodine and silver nitrate solutions with starch paste. No coloration is observed on addition, but the characteristic blue colour slowly develops.

In more concentrated solutions than it is possible to obtain by using aqueous solutions of iodine, the reaction between silver nitrate and the halogen still proceeds through the hypoiodite stage to the iodate. This can be demonstrated by the following experiment. A $N/20$-iodine solution in $N/10$-potassium iodide was treated with an amount of standard silver nitrate sufficient to remove the potassium iodide as silver iodide and to allow two molecules of the silver salt to react with each molecule of iodine present. Even in such concentrated solutions, in which obviously the decomposition of hypoiodite is greatly accelerated, it was possible to show the presence, immediately after reaction, of 5 to 10 per cent. of the total hypoiodite required by theory. The variation in the amount titrated varied with the rapidity with which the reaction was effected.

*Silver Acetate and Iodine.*—With silver acetate, iodine reacts in the same manner as with silver nitrate. One molecule of iodine in aqueous solution reacts with a molecule of silver acetate, the resulting solution, tested immediately, containing 97 per cent. of the theoretical amount of hypoiodite. With the materials present in the ratio of one molecule of iodine to two molecules of silver salt, immediate titration showed the presence of 90 per cent. of the theoretical amount.

Time reactions with silver acetate present in the ratios of 1·1 and 2 molecules respectively for each molecule of iodine gave the following results:

| | Percentage hypoiodite with 1 molecule iodine and | |
|---|---|---|
| Time. | 1·1 mols. silver acetate. | 2 mols. silver acetate. |
| 1 | 94·7 | 69·5 |
| 3 | — | 60·7 |
| 6 | 69·3 | 51·5 |
| 11 | 60·1 | 38·2 |
| 16 | 52·4 | 30·9 |
| 22 | — | 27·2 |
| 36 | 50·8 | — |
| 50 | — | 15·6 |
| 76 | 49·3 | — |

The possibility of following, from the point of view of reaction kinetics, this decomposition of hypoiodite into iodide and iodate is at present the subject of investigation by the author.

### *Summary.*

Iodine reacts with silver salts in a manner analogous to that observed in reactions with chlorine and bromine to yield insoluble silver iodide, hypoiodous acid, and another acid. The reaction occurring may be represented by the equation:

$$AgX + I_2 + H_2O = AgI + HIO + HX.$$

Owing to the instability of hypoiodous acid a second reaction occurs, accelerated by rise of temperature, increase in concentration, or presence of soluble silver salts, in which reaction the hypoiodous acid is converted into iodide and iodate. This secondary reaction may be generally represented by the equation:

$$3HIO + 3AgX = 2AgI + AgIO_3 + 3HX.$$

The simple equation of Birnbaum and of Normand and Cumming,

$$3I_2 + 3H_2O + 6AgX = 5AgI + AgIO_3 + 6HX,$$

represents the sum of the two preceding equations.

In conclusion, I wish to express my indebtedness to Prof. Henry Bassett, of University College, Reading, for his valuable assistance and advice during the course of this research.

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## VII.—*Diphenylene. Part II.*

By JAMES JOHNSTON DOBBIE, JOHN JACOB FOX, and ARTHUR JOSIAH HOFFMEISTER GAUGE.

IN previous papers dealing with the preparation and properties of 2 : 2′-dibromodiphenyl it was shown that the action of sodium on this substance results in the formation of the hydrocarbon diphenylene, $C_{12}H_8$ (T., 1911, **99**, 683, 1617). In the experiments by which this substance was first obtained the sodium was employed in the form of thin slices. The reaction proceeded slowly, but gave only a small quantity of by-products. The amount of these was reduced by substituting light petroleum for ether, whereas it was increased by the use of benzene, probably because of the ready solubility of the by-products in this medium. By using finely-divided sodium the rate of the reaction was increased, but the yield of diphenylene was greatly reduced owing to the formation of compounds of high molecular weight. One of these was found by analysis and determination of the molecular weight to have the formula $C_{84}H_{56}Br_2$.

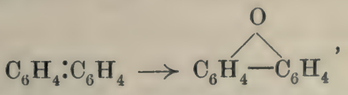
We have made numerous experiments in the hope of finding a more convenient method for the preparation of diphenylene, but so far without success. In one of these attempts *o*-di-iodobenzene was heated with copper powder, both in air and in closed exhausted tubes to 250°. Only resinous products were obtained, from which no diphenylene could be isolated, although there was reason to believe that a small quantity had been formed. Silver diphenate suggested itself as another possible starting point for the preparation of diphenylene. On subjecting this salt to dry distillation it was observed that at a particular temperature sudden decomposition set in, accompanied by much charring and a violent evolution of carbon dioxide. The distillate condensed to a mass of yellow crystals, which dissolved almost completely in light petroleum.

This solution deposited pale yellow crystals, which on recrystallisation melted at 92°. The crystals agreed in character with the lactone described by Graebe and Schestakov (*Annalen*, 1895, **284**, 316) under the name of "biphenylmethylolid," $\overset{|}{C}_6H_4\cdot C_6H_4\cdot CO\cdot\overset{|}{O}$, and by Griess (*Ber.*, 1888, **21**, 981) and Richter. Bromination of the crystals resulted in the formation of the bromo-derivative melting at 194° prepared by Richter (*J. pr. Chem.*, 1883, [ii], **28**, 294). Their identity with the lactone derived from *o*-hydroxydiphenylcarboxylic acid is therefore established. The mother liquors from this substance were evaporated to dryness and distilled in a current of steam, when crystals of pure diphenyl were obtained. No trace of diphenylene was found in these operations.

To obtain a supply of material for the further examination of the reactions of diphenylene we were compelled to revert to the original method of preparation described in our first paper on the subject. We have been obliged in consequence to limit our investigation for the present to a few of the simpler derivatives. A *dinitrodiphenylene* was obtained by heating diphenylene with diluted nitric acid under pressure. By the action of the fuming acid a *tetranitro*-derivative was formed. Considerable loss of material occurred in both cases, resinous and waxy substances being formed, which were not sufficiently well defined for investigation. Bromine reacted with diphenylene with the formation of two products, namely, 2:2′-dibromodiphenyl and a *dibromodiphenylene.* By the oxidation of the latter, *p*-bromobenzoic acid was obtained, together with an acid which yielded a strongly fluorescent solution when condensed with resorcinol. The formation of *p*-bromobenzoic acid indicates that under the conditions described substitution takes place in the meta-position with respect to the middle ring.

The behaviour of diphenylene when heated with diluted nitric acid is of special interest. From the products of the reaction three definite substances were isolated, namely, (1) a dinitrodiphenylene, (2) diphenylene oxide, and (3) a nitrophthalic acid. In addition, a quantity of waxy matter of indefinite character was formed.

It is quite clear from the production of diphenylene oxide by the oxidation with dilute nitric acid, on the one hand,



$$C_6H_4{:}C_6H_4 \longrightarrow \overset{O}{C_6H_4{-}C_6H_4},$$

and from the regeneration of 2:2′-dibromodiphenyl on the other, $C_6H_4{:}C_6H_4 \longrightarrow C_6H_4Br\cdot C_6H_4Br$, that the diphenylene molecule is rather unstable. It is probably owing to this instability that diphenylene forms waxy substances so readily under the influence of various reagents, and that the formation of substitution derivatives is accompanied by so much loss of material.

## EXPERIMENTAL.

Finely divided sodium was immersed in dry ether, and dried 2 : 2′-dibromodiphenyl was added. An immediate reaction resulted, the solution became deep brown, and a quantity of red, insoluble matter separated. The reaction was complete in a very short time. The ether and suspended solid matter were separated from unchanged sodium, and the ethereal liquid was filtered. When the insoluble matter was boiled with a little water to remove sodium bromide a yellow powder was left behind. This dissolved readily in cold benzene and chloroform, from the solution in which it could be precipitated by light petroleum or alcohol. The substance was readily purified by repeated treatment with a mixture of benzene and light petroleum, from which it separated as an amorphous, yellow powder, melting and decomposing at 306°:

0·1246 gave 0·3756 $CO_2$ and 0·0532 $H_2O$. C = 82·2; H = 4·7.
0·1036 „ 0·0312 AgBr. Br = 12·8.
0·2876 in 18·74 benzene gave E = 0·037. M.W. = 1180.
$C_{84}H_{56}Br_2$ requires C = 82·3; H = 4·6; Br = 13·1 per cent.
M.W. = 1224.

The formula of this substance may be written $(C_{12}H_8)_7Br_2$ when it is seen to be derived from the action of sodium on two molecules of 2 : 2′-dibromodiphenyl, the product of which then reacts with a third molecule, and so on until the compound having eighty-four carbon atoms is reached, which is insoluble in ether. The compound $C_{84}H_{56}Br_2$ is similar in character to the compound $C_{78}H_{52}Br_2$ described by Goldschmiedt (*Monatsh.*, 1886, **7**, 40) and Hosaeus (*ibid.*, 1893, **14**, 323), which results from the action of sodium on the various dibromobenzenes. The ethereal filtrate from the compound $C_{84}H_{56}Br_2$ contains the diphenylene formed in the reaction, together with other substances similar in character to $C_{84}H_{56}Br_2$, but soluble in ether. These may be readily separated from diphenylene by taking advantage of their insolubility in light petroleum or in cold alcohol.*

*Bromination of Diphenylene.*—The diphenylene to be operated on was covered with water, four times its weight of bromine was added a little at a time, and the whole mass ground up in a mortar. No perceptible rise of temperature resulted, and only a small amount of hydrogen bromide was evolved. The whole mass was treated with dilute aqueous sodium hydroxide solution until all the unchanged bromine was removed, the residual solid collected, washed with water and a little alcohol, and dissolved in benzene. Colourless needles separated, which did not melt sharply, but after a second crystallisation melted at 80°. This substance was identical with 2:2′-dibromodiphenyl formerly described by us (T., 1911, **99**, 1618). The mother liquors on concentration deposited further crops of crystals, of which the first fractions, judging from the low melting point, contained more 2:2′-dibromodiphenyl. The last fractions consisted chiefly of a substance which melted after several crystallisations at 171°, and had the composition of *dibromodiphenylene*:

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* The behaviour and properties of these substances are not described here, as they have no bearing on the derivatives of diphenylene.

0·1330 gave 0·1624 AgBr. Br = 52·0.
$C_{12}H_6Br_2$ requires Br = 51·6 per cent.

The yield of pure substance was not more than 30 per cent., a large proportion of the diphenylene operated on having been converted into 2:2′-dibromodiphenyl and waxy substances of indefinite character containing halogen. Dibromodiphenylene dissolves fairly readily in benzene and alcohol, from which it separates in long, stout, colourless needles. When oxidised by chromic acid it yields a mixture of acids. One of these was recognised as a phthalic acid by the strongly fluorescent solution obtained by condensing it with resorcinol. The other was proved by its equivalent weight and melting point (248°) to be *p*-bromobenzoic acid.

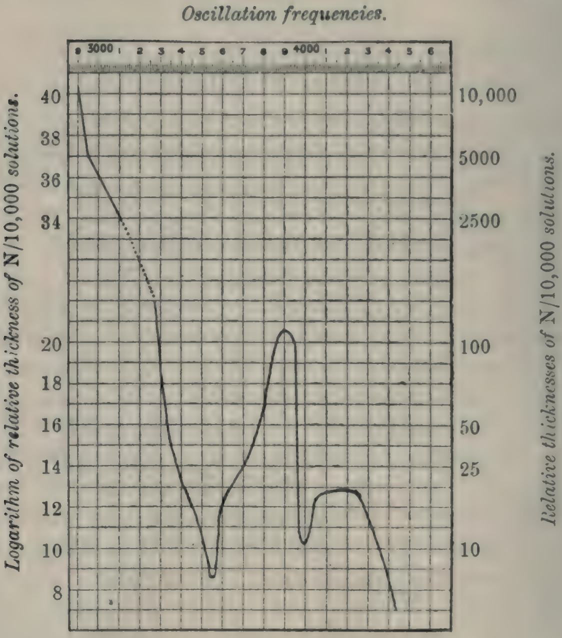
*Nitration of Diphenylene.*—One part of diphenylene was dissolved in ten parts of concentrated sulphuric acid, and the mixture cooled with ice; four parts of nitric acid (D 1·5) were then added a little at a time, keeping the whole immersed in a freezing mixture. When the action, which at first was very violent, had moderated, the flask containing the mixture was heated on a water-bath for one hour. The contents of the flask after being allowed to cool were poured into ten times their volume of ice-water; the solid which separated was collected, washed with water and a little alcohol, and dried. The yield of crude solid was about 30 per cent. of the weight of the diphenylene taken. The dried precipitate was boiled with a large quantity of alcohol, from which it crystallised on cooling in fine, yellow needles, melting at 223°:

0·2372 gave 0·3768 $CO_2$ and 0·0304 $H_2O$. C = 43·3; H = 1·4.
0·1038 „ 15·1 c.c. $N_2$ at 19·5° and 768 mm. N = 17·1.
$C_{12}H_4O_8N_4$ requires C = 43·4; H = 1·2; N = 16·9.

The substance is therefore a *tetranitrodiphenylene*. It dissolves sparingly in alcohol and glacial acetic acid, but is almost insoluble in other organic solvents.

## *Action of Diluted Nitric Acid on Diphenylene.*

Diphenylene was heated in a sealed tube for sixteen hours at 150° with twenty times its weight of diluted acid (D 1·2). Considerable decomposition resulted, and a yellow, semi-crystalline mass remained. This was washed with water, digested with ether, and finally with alcohol and benzene. The residue obtained after this treatment consisted of pale yellow needles, which dissolved sparingly in alcohol. It separated from its alcoholic solution in small needles melting at 204°. Analysis showed that the substance was a *dinitrodiphenylene*. The yield was small. Dinitrodiphenylene is almost insoluble in ether, benzene, or carbon disulphide, but dissolves sparingly in alcohol, acetone, or glacial acetic acid:



*Diphenylene oxide in alcohol.*

0·1236 gave 0·2678 $CO_2$ and 0·0334 $H_2O$. C = 59·1; H = 3·0.
0·1314 „ 13·4 c.c. $N_2$ at 17° and 761 mm. N = 11·8.
$C_{12}H_6O_4N_2$ requires C = 59·5; H = 2·5; N = 11·6 per cent.

The ethereal solution was treated with aqueous sodium hydroxide, whereby a small amount of an acid was removed. On evaporating off the ether a waxy mass was left behind, which was redissolved in alcohol. From the alcoholic solution small plates deposited. On redissolving these plates and treating with picric acid, a picrate separated out from the concentrated alcoholic solution, which on recrystallisation melted at 95°. By acting on the picrate with aqueous sodium hydroxide and extracting the resulting liquid with ether a crystalline solid was obtained melting at 78—79°, and possessing the properties of diphenylene oxide. Its identity with this substance was clearly established by its melting point, the melting point of its picrate, and by its absorption spectrum. The absorption spectrum of diphenylene oxide (see diagram) is strikingly characteristic. It possesses two bands; the head of the larger and more persistent band is at $1/\lambda$ 3530, and of the small narrow band at $1/\lambda$ 4000. The spectrum of the substance from diphenylene is identical with this.

The aqueous liquid remaining after the reaction contained an acid which was purified by means of its sodium salt. It corresponded in molecular weight and in the melting point of its methyl ester with 3-nitrophthalic acid (Ag salt: Found, Ag=49·9. Calc., Ag=50·5 per cent.).

We hope in a future paper to give a more particular account than has yet been possible of the physical properties of diphenylene.

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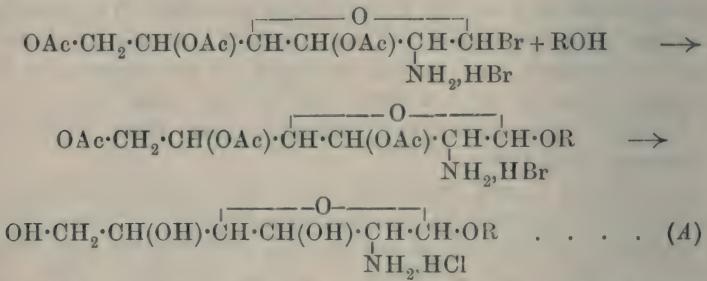
# VIII.—*Synthetical Aminoglucosides Derived from* d-*Glucosamine.*

By James Colquhoun Irvine and Alexander Hynd, M.A., B.Sc. (Carnegie Fellow).

The action of acyl bromides on glucosamine, which was first studied in this laboratory four years ago, has opened up the way for the preparation of glucosamine derivatives of a new type. We have already in previous papers (T., 1911, **99**, 250; 1912, **101**, 1128) described the use of bromotriacetylglucosamine hydrobromide in the preparation of α-aminomethylglucoside (methylglucosamine), and in the present paper it is shown that the bromo-compound functions as a general synthetic reagent, by means of which the glucosamine residue may be coupled with any hydroxy-compound possessing the requisite solubilities. In this way synthetic aminoglucosides may be prepared, which can be regarded either as derivatives of glucosamine or of glucose.

Expressed in the simplest general terms, the reaction involved consists in the condensation of bromotriacetylglucosamine hydrobromide with a hydroxy-compound in presence of a base which combines with the liberated hydrogen bromide. The product of this first reaction is the salt of a triacetylated aminoglucoside, from which the acyl groups are removed by heating with a dilute solution of hydrogen chloride in methyl alcohol. The most obvious interpretation of the changes is shown in the following scheme:

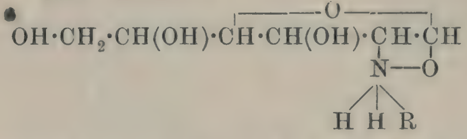


$$\mathrm{OAc{\cdot}CH_2{\cdot}CH(OAc){\cdot}\overbrace{CH{\cdot}CH(OAc){\cdot}\underset{NH_2,HBr}{CH}{\cdot}CH}^{O}Br + ROH} \longrightarrow$$

$$\mathrm{OAc{\cdot}CH_2{\cdot}CH(OAc){\cdot}\overbrace{CH{\cdot}CH(OAc){\cdot}\underset{NH_2,HBr}{CH}{\cdot}CH}^{O}{\cdot}OR} \longrightarrow$$

$$\mathrm{OH{\cdot}CH_2{\cdot}CH(OH){\cdot}\overbrace{CH{\cdot}CH(OH){\cdot}\underset{NH_2{\cdot}HCl}{CH}{\cdot}CH}^{O}{\cdot}OR} \quad . \quad . \quad . \quad . \quad (A)$$

but in the particular case of α-aminomethylglucoside we indicated that the simple general formula of the type (*A*) cannot be reasonably applied to the compound, and we suggested the following variation, which includes a modified betaine ring in the molecule:



$$\mathrm{OH{\cdot}CH_2{\cdot}CH(OH){\cdot}\overbrace{CH{\cdot}CH(OH){\cdot}\underset{\underset{H\ H\ R}{N}}{CH}{\cdot}\underset{O}{CH}}^{O}} \quad . \quad . \quad . \quad . \quad (B)$$

It appeared to us of interest to prepare a number of aminoglucosides on account of their possible importance as a first step in developing the synthetical chemistry of the glucoproteins, and to ascertain if both types (*A*) and (*B*) can exist.

The conclusion arrived at is that, when the group condensed with the glucosamine residue consists of a short open chain, the product possesses properties similar to those of α-aminomethylglucoside, and thus belongs to the type (*B*). On the other hand, the derivatives of glucosamine which contain a benzene nucleus in the glucosidic position do not differ essentially from true glucosides, except in so far as the properties of the compounds are modified by the presence of the basic amino-group. As examples of this class, to which the general formula (*A*) applies, we have α-aminobenzylglucoside, α-aminosalicin, α-aminohelicin, and α-aminomorphineglucoside.

So far, then, as generalisations may be made from the data now available, the aminoglucosides related to glucosamine may be divided into the above two classes, which differ sharply in their properties. Those in which nitrogen is linked to oxygen are remarkably stable towards the hydrolytic action of hydrogen chloride; they are also unaffected by emulsin, and form additive compounds with silver iodide. In sharp contrast to this behaviour, the normal glucosides are easily hydrolysed by acids, and in the case of aminohelicin and aminosalicin are apparently also hydrolysed by emulsin. The general question of the action of enzymes on compounds of both types now described is evidently important, and Prof. H. E. Armstrong has kindly undertaken to extend our experiments in this direction.

Unfortunately, no definite description can be given of the working methods employed to prepare aminoglucosides from bromotriacetylglucosamine hydrobromide, as the process has to be modified to suit each individual case. Reference to the experimental part will show that when the hydroxy-compound to be coupled with the glucosamine residue is a volatile liquid, it should be used in large excess. With liquids of high boiling points, on the other hand, it is necessary to restrict the amount used to one molecular proportion so as to avoid, as far as possible, the inevitable decomposition of the product which results during the removal of the excess of the reagent. With solid hydroxy-compounds, ether, chloroform, or other indifferent solvent may be employed, but in such cases the base used must also be soluble.

The use of bromotriacetylglucosamine hydrobromide is, in fact, beset with difficulties. Owing to the instability of the compound, its limited range of solubility, and the fact that it cannot be employed in solution at temperatures exceeding 60°, its use in synthetical work is much more restricted than that of tetra-acetylbromoglucose. Even in successful reactions the yields obtained were in most cases small owing to the difficulty experienced in removing deliquescent by-products. In the following tables lists are given of the aminoglucosides and their constants, the nomenclature employed expressing the relationship of the compounds to *d*-glucose:

### TABLE I.

*Acetylated Aminoglucosides.*

| | Decomposition temperature. | $[\alpha]_D^{20^\circ}$ in methyl alcohol. | Type. |
|---|---|---|---|
| Triacetyl-α-aminomethylglucoside (HBr) *. | 230—233° | +20·26° | (*B*) |
| Triacetyl-α-aminoethylglucoside (HBr)...... | 250—251 | 12·46 | (*B*) |
| Triacetyl-α-aminoamylglucoside (HBr)...... | 227° | 10·38 | (*B*) |
| Triacetyl-α-aminobenzylglucoside (HBr) .. | 235—236 | 52·1 | (*A*) |
| Triacetyl-α-aminohelicin (HBr) ............... | 215—216 | 200° → +43·6 | (*A*) |

* T., 1911, **99**, 250.

### TABLE II.

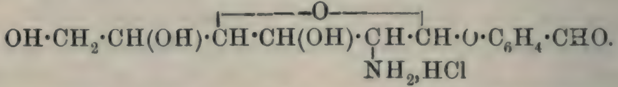
*Aminoglucosides.*

| | Decomposition temperature. | $[\alpha]_D^{20^\circ}$ in water. | Type. |
|---|---|---|---|
| α-Aminomethylglucoside hydrochloride* ... | 190° | –24·2° | (*B*) |
| α-Aminoethylglucoside ,, ... | 213—214 | 27·75 | (*B*) |
| α-Aminobenzylglucoside ,, ... | 176 | 51·15 | (*A*) |
| α-Aminohelicin ,, ... | 180 | 8·97 | (*A*) |
| α-Aminosalicin ,, ... | 178—179 | 18·99 | (*A*) |
| α-Aminomorphineglucoside .................. | 246—248 | 113·45 | (*A*) |

* T., 1911, **99**, 250.

In addition to the above, a number of cases were examined in which condensation occurred, but the product could not be isolated in the pure state.

Probably the most important compounds now described are the salts of α-amino-*o*-aldehydophenylglucoside and α-aminosaligeninglucoside, and the constitution of each was accordingly determined so as to establish their relationship with the natural glucosides helicin and salicin. We find that in α-amino-*o*-aldehydophenylglucoside both the amino- and aldehydic groups remain intact; the compound, moreover, has no phenolic or reducing properties. This at once limits the constitution to the formula:



$$OH\cdot CH_2\cdot CH(OH)\cdot \overset{|\!-\!-\!-\!-O-\!-\!-\!-|}{CH\cdot CH(OH)\cdot \underset{NH_2,HCl}{CH}\cdot CH}\cdot O\cdot C_6H_4\cdot CHO.$$

The compound is thus to be regarded as the hydrochloride of α-aminohelicin. At the same time attention should be drawn to the fact that the observations made on the rotatory power of triacetyl-α-aminohelicin seem at first sight in disagreement with this view. The account of this optical behaviour is here given in detail, as an indication of the caution with which changes in rotation must be accepted as a proof of reversible isomeric change.

### *Pseudo-mutarotation of Triacetyl-α-aminohelicin Hydrobromide.*

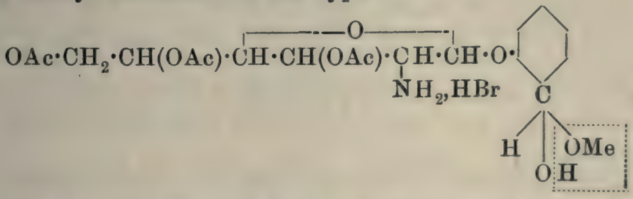
In contrast with the other aminoglucosides examined, the compound now under consideration showed curious optical changes in solution resembling closely those displayed by reducing sugars. When dissolved in methyl alcohol the specific rotation was initially dextro, but rapidly diminished on keeping. An idea of the magnitude and speed of the change can be gained from the following observations:

$c=1{\cdot}4943,\ l=2,\ t=20°.$

| Time from the first reading. | | $\alpha$. | $[\alpha]_D^{20°}$. |
|---|---|---|---|
| Minutes | 0 | +5·98° | +200·09° |
| ,, | 25 | 5·88 | 196·7 |
| ,, | 90 | 5·04 | 168·6 |
| ,, | 255 | 3·93 | 131·5 |
| Hours | 28 | 2·44 | 81·63 |
| ,, | 65 | 1·75 | 58·54 |
| ,, | 1500 | 1·30 | 43·49 (constant) |

The curve illustrating the complete optical change was different from the records usually obtained in the case of true mutarotation, in that the initial fall was slow compared with the normal steepness of the curve. Two reactions, one resulting in a slight rise and the other in a pronounced fall in rotatory power, thus appear to proceed simultaneously. The solvent was removed, under the ordinary pressure, from a solution which had attained the permanent rotatory power, and, on the addition of petroleum of low boiling point, the original compound was precipitated in the crystalline state unaltered in melting point and composition. On redissolving this specimen in methyl alcohol the above optical changes were repeated, the solution once more showing downward mutarotation. This behaviour might reasonably be interpreted as indicating that the reducing group of the glucosamine residue had remained unsubstituted, and was thus undergoing the usual $\alpha \rightleftharpoons \beta$ transformation in solution; the precipitation by petroleum in such a case would cause the separation of the less soluble labile form.

We are of the opinion, however, that the rotatory changes referred to are due to temporary combination with the solvent to form a methyl alcoholate of the type:



which readily loses methyl alcohol in the manner indicated by the dotted line. This is supported by the fact that evaporation at 10°/12 mm. of a solution which had attained the permanent rotatory power ($[\alpha]_D$ +43°) gave no crystalline product, but a colourless syrup. A portion of this syrup was preserved in a vacuum desiccator for several weeks, when it gradually solidified to a mass of crystals consisting of the original compound. The remainder of the syrup was dried at 40°/15 mm. until constant in weight. A Zeisel estimation then gave OMe=5·00, the theoretical value for the methyl alcoholate formulated above being OMe = 5·9 per cent. Evidently a small amount of the combined methyl alcohol had been expelled during the drying process, and this view was confirmed by the fact that the analysis specimen showed slight mutarotation in the downward sense on being re-dissolved in methyl alcohol. These changes are summarised below, the values being calculated on the concentration of the glucoside salt used:—

| Initial $[\alpha]_D$. | | Permanent $[\alpha]_D$. | | $[\alpha]_D$ After drying. | | Second permanent $[\alpha]_D$. |
|---|---|---|---|---|---|---|
| +200·1° | → | +43·5° | → | +73·6° | → | +43·8° |
| (OMe = Nil). | | | | (OMe = 5·0 per cent.). | | |

Considerable support was given to this explanation by the fact that aqueous solutions of triacetyl-α-aminohelicin hydrobromide showed a constant rotation when preserved for a week.

### *Possible Relationship of Aminoglucosides to Glucoproteins.*

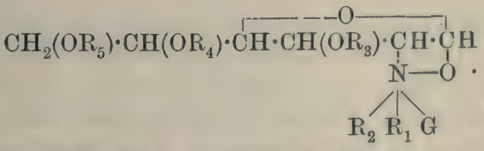
So far, no simple aminoglucosides of the nature of the compounds described in this paper have been isolated from natural sources, but nevertheless it is highly probable that substances of this type do actually exist in nature. At the present time considerable attention is being directed to the study of the simpler nitrogenous constituents of plants, and the recent work of Schultze and his pupils (*Zeitsch. physiol. Chem.* 1912, **79**, 235, and previous papers) has shown that betaine and complexes containing ring structures similar to betaine are far from being unique, and are widely distributed. Moreover, the proofs given by van Romburgh and Barger of the constitution of hypaphorine, and by Barger and Ewins of the structure of ergothioneine (T., 1911, **99**, 2068, 2336), afford additional examples that betaine complexes of different types must now be regarded as forming a distinct class of natural products.

Presumably natural aminoglucosides which possess a betaine-like structure are most likely to occur in organisms in which chitin is deposited as a protective layer, and we have accordingly commenced a systematic search for such compounds in the fungi.

It is also evident that aminoglucosides, derived from glucosamine, possess a special interest, as they may be closely related to glucoproteins. It is true, as Abderhalden has stated, that in the particular case of betaine the compound seems to play no specific part in the protein molecule, and is not likely to be encountered in protein cleavage products. Schultze, who agrees with this view, holds that betaine derivatives resemble alkaloids which, when once formed, take no further part in plant reactions. These statements, however, do not seem applicable to the betaine-like or glucosidic derivatives of glucosamine where the existence of the potential amino-group and three hydroxyl groups naturally confers considerable reactivity on the molecule.

A review of the somewhat scanty and diffuse information regarding glucoproteins shows that there is at least a strong probability that they are closely related to aminoglucosides, and suggests the possibility of synthesising complexes which would bear the same relationship to glucoproteins that synthetic polypeptides do to proteins; thus the fact that mucins, when boiled with 2·5 per cent. hydrogen chloride, undergo only partial hydrolysis to give non-reducing intermediate products which are only converted into glucosamine when the hydrolysis is carried out by more concentrated acid, has given rise to considerable discussion. The reaction, however, seems capable of a simple explanation. Hitherto it has been held that this behaviour is a proof that the amino-sugar is not present as such in the protein molecule, but is formed as a decomposition product. Our results on the hydrolysis of acetylated aminoglucosides of the type (*B*) offer a remarkable parallel to this behaviour, as treatment with 2·5 per cent. hydrochloric acid removes only the substituting acyl groups, and leaves the "glucosidic" residue unaffected. The action of alkalis on the two classes of compound also shows marked similarity. Acetylated aminoglucosides are thus deprived of the acyl groups only, and in the case of glucoproteins the hydrolysis is likewise only partial, and gives non-reducing products. It would thus appear that in the glucoproteins amino-acyl residues occupy the amino-position, and possibly also all the hydroxyl positions with the exception of the glucosidic group. Inspection of the available data on the reactions of glucoproteins seems to us to indicate that at all events some of these compounds may be regarded as analogues of triacetyl-α-aminomethylglucoside, in which the substituting groups are amino-acyl residues, and according to this view the structure would fall into line with Fischer's constitution for tannin (*Ber.*, 1912, **45**, 915).

A general formula of this type would be represented by the expression:



$$\mathrm{CH_2(OR_5)\cdot CH(OR_4)\cdot \overset{\ulcorner\text{———O———}\urcorner}{CH\cdot CH(OR_3)\cdot \underset{\underset{R_2\;R_1\;G}{N—O}}{CH\cdot CH}}}\ .$$

where G represents the glucosidic group, and $R_1$, $R_2$, etc., stand for amino-acyl residues, which are probably short polypeptide chains. A complex of the above type would give, on hydrolysis with dilute hydrogen chloride, the amino-acids corresponding with $R_1$, $R_2$, etc. The latter would also be removed by the action of alkalis, but the residue G would be much more stable to both acids and alkalis.

Consideration of (1) the average carbon, hydrogen, and nitrogen contents of the mucins, (2) the number and amount of the amino-acids formed from them on hydrolysis, and (3) the relative yield of glucosamine salt produced in each case, shows that the above structure is in satisfactory agreement with experimental data.

An alternative structure for the mucins may, however, be considered, namely, that a complex polypeptide chain is simply attached to the glucosamine residue through the amino-group. This structure seems highly unlikely, as not only would the compounds show reducing powers, but hydrolysis in definite stages by means of acids would be less likely to occur, and could in no case give a glucoside. Moreover, it is difficult to imagine, in the case of a long side-chain of this description, that condensation with the free hydroxyl groups would not occur.

The above considerations as to the structure of gluco-proteins are, of course, largely speculative, but are given here in view of the recent appearance of a preliminary note by Hopwood and Weizmann (P., 1912, **28**, 261), who describe the action of certain bromoacyl haloids on glucosamine, the obvious extension of their work being the formation of aminoacyl derivatives of the amino-sugar. We think it only right to state here that, during the past two years, workers in this laboratory have also been engaged in introducing bromoacyl residues into glucosamine. Our investigations are, however, directed to the preparation of complexes in which the glucosidic and hydroxyl groups, as well as the amino-group, are substituted, and we take this opportunity of stating that syntheses of the nature indicated in the above theoretical discussion are being vigorously prosecuted.

## EXPERIMENTAL.*

### *Acetylated Aminoglucosides.*

### *Condensation of Bromotriacetylglucosamine Hydrobromide with Ethyl Alcohol.*

Triacetyl-α-aminoethylglucoside was, in the first instance, prepared by dissolving bromotriacetylglucosamine hydrobromide (1 mol.) in ethyl alcohol (3 mols.) and pyridine (1 mol.). Although the yield of crude condensation compound thus obtained was quite satisfactory, the removal of the deliquescent by-products proved to be so troublesome that the method was abandoned in favour of the following process.

---

* All the reagents employed were pure and were specially dried before use. Except where otherwise stated, evaporations and concentrations were conducted under diminished pressure.

11·7 Grams of the crude bromo-compound, which, as explained in a previous paper (*loc. cit.*), should contain 10 grams of the pure substance, were extracted with excess of cold ethyl alcohol, and the solution filtered from glucosamine salts. Meanwhile, a solution of 6·3 grams of dry morphine in ethyl alcohol had been prepared, and the two solutions were then mixed without delay. The separation of the morphine hydrobromide began in a few minutes, and was complete in twelve hours. Only slightly less than the theoretical amount of the morphine salt was thus obtained. The filtered liquid on concentration yielded two crops of crystalline product, and even the final mother liquor on evaporation to dryness gave a crystalline residue. The total yield was almost quantitative.

After recrystallisation from a concentrated solution in ethyl alcohol, the product was washed with cold alcohol and then with ether. The material used in the following determinations was dried in a vacuum until constant in weight.

Found: C=40·42; H=5·86; Br=19·30; OEt=10·68.

$C_{12}H_{18}O_7N{\cdot}OEt,HBr$ requires C=40·56; H=5·84; Br=19·30; OEt=10·87 per cent.

*Triacetyl-a-aminoethylglucoside hydrobromide* forms colourless needles, which begin to turn brown at 220°, and melt, with complete decomposition, at 250°. The compound gives a very sharp glucosidic reaction with Fehling's solution, and is only hydrolysed into its constituents when boiled with concentrated aqueous hydrogen chloride. Like the other compounds of this type, it is dextrorotatory:

*Solvent: Methyl Alcohol.* $c=1{\cdot}806$, $l=2$, $\alpha+0{\cdot}45°$, $[\alpha]_D^{20}$ $+12{\cdot}5°$.

Any variation of the method of preparation just described is liable to give complex, uncrystallisable syrups; thus, for example, the use of dry acetone in sufficient amount to dissolve the bromo-compound gave rise to considerable decomposition, the substitution of silver carbonate for morphine gave a similar result, and all attempts to carry out the condensation in absence of a base merely regenerated glucosamine hydrobromide.

### *Condensation of Bromotriacetylglucosamine Hydrobromide with Amyl Alcohol.*

In this particular instance, the condensation is unsuccessful when morphine is used to remove hydrogen bromide. Ten grams of the bromo-compound (1 mol.) were mixed with 5·28 grams of amyl alcohol (3 mols.) containing 1·50 grams of pyridine (1 mol.). On vigorous shaking, the bulk of the material passed into solution, and, after forty-five minutes, the liquid set to a stiff paste. The reaction was complete in two hours. The solid product, after removal of the excess of amyl alcohol by draining on porous porcelain, was extracted with ethyl alcohol, and the solution, after filtration from glucosamine salts, concentrated in a vacuum desiccator. The product then separated in the crystalline state, and was purified by recrystallisation from ether containing 40 per cent. of ethyl alcohol.

The yields obtained by this process were never more than 20 per cent. of the theoretical amount, and were not improved by any modifications of the method.

Found: $C=44{\cdot}52$; $H=6{\cdot}72$; $Br=17{\cdot}53$.

$C_{12}H_{18}O_7N{\cdot}O{\cdot}C_5H_{11},HBr$ requires $C=44{\cdot}71$; $H=6{\cdot}63$; $Br=17{\cdot}52$ per cent.

*Triacetyl-α-aminoamylglucoside hydrobromide* crystallises readily in delicate needles from solutions in ethyl acetate, amyl alcohol, or a mixture of ether and alcohol. The compound, however, shows a marked tendency to separate in a gelatinous form, which only becomes crystalline when stirred with dry ether. The crystals turn brown at 217°, and decompose at 227°. The compound behaves as a glucoside towards Fehling's solution, but is remarkably stable to hydrolysis. Contrary to expectation, all attempts to remove the acetyl groups resulted in profound decomposition, and thus the unsubstituted glucoside was not isolated.

The specific rotation in methyl alcohol for $c=1{\cdot}687$ was $+10{\cdot}4°$. It should here be stated that the amyl alcohol used in the preparation of this glucoside showed $\alpha\ -0{\cdot}76°$ for $l=1$. The excess of amyl alcohol which remained uncombined was recovered from the tiles and purified. It then showed no appreciable alteration in rotatory power from the original value.

### *Condensation of Bromotriacetylglucosamine Hydrobromide with Benzyl Alcohol.*

The preparation of triacetyl-α-aminobenzylglucoside presented considerable difficulty, and the following process, although far from satisfactory, was the only one to give a crystalline product:

Eighteen grams of the pure recrystallised bromo-compound (1 mol.) were gradually mixed with 4·32 grams of benzyl alcohol (1 mol.), containing 3·18 grams of pyridine (1 mol.). The mobile, syrupy liquid thus obtained gradually gelatinised. The mass was then thoroughly mixed with dry ether, the solvent poured away, and the residue dissolved in chloroform. On the cautious addition of carbon tetrachloride an oil was precipitated, which was extracted with a mixture of alcohol and benzene. The product crystallised slowly from this solution. Several recrystallisations from a mixture of ether (3 parts) and alcohol (1 part) were necessary to obtain the glucoside salt in a state of purity. The yield was less than 1 gram.

Found: C=47·65; H=5·69; Br=16·63.

$C_{12}H_{18}O_7N\cdot O\cdot C_7H_7,HBr$ requires C=47·88; H=5·50; Br=16·79 per cent.

*Triacetyl-a-aminobenzylglucoside hydrobromide* melts and decomposes at 235—236°. It does not reduce Fehling's solution, but is readily hydrolysed, and is thus a normal glucoside. The compound is completely decomposed when heated with barium hydroxide solution.

*Solvent: Methyl Alcohol.* $c=1{\cdot}372$, $l=2$, $t=20°$, $\alpha+1{\cdot}43°$, $[\alpha]_D^{20}+52{\cdot}11°$.

### *Condensation of Bromotriacetylglucosamine Hydrobromide with Salicylaldehyde.*

The success of this reaction is entirely dependent on the purity of the materials employed. The purest salicylaldehyde obtainable from Kahlbaum was used, and the bromo-compound was recrystallised until quite colourless. Thirteen grams of triacetylbromoglucosamine salt (1 mol.) were suspended in dry ether containing 2·3 grams of anhydrous pyridine (1 mol.). A solution of 10·8 grams of salicylaldehyde (3 mols.) in dry ether was then quickly added, and the mixture vigorously shaken for an hour, during which time the sides of the bottle became coated with a yellow oil. The clear liquid was poured off, and diluted with petroleum of low boiling point until no further precipitate was formed. In this way the glucoside salt was obtained in excellent yield in golden-yellow needles, which were purified by solution in ether and precipitation with petroleum.

Found: C=46·60; H=4·92; Br=16·40; N=2·91.

$C_{12}H_{18}O_7N\cdot O\cdot C_6H_4\cdot CHO,HBr$ requires C=46·51; H=4·94; Br=16·32; N=2·86 per cent.

*Triacetyl-a-amino-o-aldehydophenylglucoside hydrobromide*, when pure, is quite white, but the crystals are usually faintly yellow. The compound begins to turn brown at 170°, and completely decomposes at 216°. The solubility shows great variation with the degree of purity, as minute traces of salicylaldehyde render the compound freely soluble in practically all organic solvents, including ether.

The pure substance is, however, dissolved readily only by the lower alcohols, and sparingly by water. Fehling's solution is reduced only after hydrolysis, the removal of the salicylaldehyde residue taking place with extreme ease.

The constitution assigned to the compound in the introduction is deduced from the following properties. When suspended in nitrous acid solution, nitrogen is evolved, thus indicating the presence of the amino-group. That the compound is a glucoside is shown by its behaviour towards Fehling's solution before and after hydrolysis, and, as a positive result was obtained with Schiff's reagent, the aromatic aldehydic group remains unsubstituted, and is not linked to the sugar residue. No definite hydrazone or oxime could, however, be isolated as the compound was decomposed by phenylhydrazine or hydroxylamine. The addition of ferric chloride to a methyl-alcoholic solution of the glucoside gave only a pale green coloration, which became violet when the solution was diluted with water, but this result was, in all probability, due to slight hydrolysis. The absence of a phenolic group was confirmed by the fact that acidification of the glucoside salt dissolved in sodium hydroxide gave no precipitate. The compound is thus regarded as the salt of triacetyl-α-aminohelicin. The pseudo-mutarotation shown by the compound in methyl-alcoholic solution is described and discussed in the introduction.

### *Unsuccessful Attempts to Prepare Acetylated Aminoglucosides from Bromotriacetylglucosamine Hydrobromide.*

The experiments summarised below refer to reactions in which, as a rule, condensation did occur, but the products could not be isolated in a pure condition in sufficient quantity for detailed examination. In each case the experimental methods employed were varied by the use of different solvents and bases, or by the substitution of sodium derivatives for the free hydroxy-compounds.

| Reagent used. | Result. |
|---|---|
| Ethylene glycol………… | Condensation occurred: product amorphous and deliquescent. |
| *l*-Menthol ……………… | Condensation occurred, but only a trace of crystalline product was isolated. |
| Saligenin ………………… | Reaction took place, but the acetyl groups were partly removed during the change. |
| Vanillin<br>Quinol } ……………… | Reaction occurred in each case. The products were, however, uncrystallisable syrups. |
| Ethyl mercaptan ……… | No reaction. |
| Phenyl mercaptan …… | No reaction. |

### *Unsubstituted Aminoglucosides.*

### *α-Aminoethylglucoside Hydrochloride.*

The preparation of this compound from triacetyl-α-aminoethylglucoside was carried out exactly as described (*loc. cit.*) in the case of the corresponding methyl compound. Unless carefully recrystallised material is used in the preparation, the product is liable to be contaminated with the salt of aminomorphineglucoside, which is subsequently described. The hydrochloride of α-aminoethylglucoside is, however, easily obtained pure by crystallisation from ethyl alcohol.

Found: C = 39·31; H = 7·44; Cl = 14·70.

$C_6H_{12}O_4N{\cdot}OEt,HCl$ requires C = 39·41; H = 7·44; Cl = 14·55 per cent.

*Solvent: Water.* $c = 2{\cdot}6850$, $l = 2$, $t = 20°$, $\alpha - 1{\cdot}49°$, $[\alpha]^{20}_{D} - 27{\cdot}75°$.

The compound resembles α-aminomethylglucoside hydrochloride very closely. It crystallises in well-formed, prismatic needles, and is insoluble in organic solvents with the exception of the lower alcohols. It possesses no definite melting point, but turns brown at 195° and decomposes at 213—214° (corr.). Towards Fehling's solution the behaviour is characteristic of a glucoside, but hydrolysis only takes place on prolonged boiling with concentrated hydrochloric acid. It may be mentioned that a 1 per cent. solution of the compound in 5 per cent. aqueous hydrogen chloride was unaffected in rotatory power by heating for ten hours at 100°.

### *α-Aminobenzylglucoside Hydrochloride.*

Owing to the difficulties experienced in obtaining pure triacetyl-α-aminobenzylglucoside hydrobromide it was necessary to modify the usual method of preparing the unsubstituted glucoside. Bromotriacetylglucosamine hydrobromide and dry morphine were mixed in molecular proportions and suspended in dry ether; a large excess (6 mols.) of benzyl alcohol was then added, and the mixture shaken for three days. The dissolved material was then precipitated by the addition of ether, and, after filtration, the solid matter was extracted with cold alcohol. The extract, on evaporation to dryness, gave a semi-crystalline residue, which was shaken with ether and filtered. The product thus obtained was not uniform, and consisted of a mixture of the salts of partly acetylated aminobenzylglucosides, but this did not interfere with the preparation of the unsubstituted glucoside. The complete removal of the acetyl groups was carried out by heating at 70° for three hours with methyl alcohol containing

2 per cent. of hydrogen chloride, and the further treatment did not differ in any essential respect from the other hydrolyses described. The crude product was purified by solution in methyl alcohol and fractional precipitation with ether.

Found: C=50·90; H=6·78; Cl=11·56.

$C_6H_{12}O_4N{\cdot}O{\cdot}CH_2{\cdot}C_6H_5,HCl$ requires C=51·03; H=6·59; Cl=11·60 per cent.

In crystalline form, solubilities, and behaviour towards Fehling's solution the compound resembles the other aminoglucosides described; it is, however, easily hydrolysed. The salt decomposes, after preliminary browning, at 176° (corr.), and shows in aqueous solution ($c=1$) the specific rotation −51·2°.

### *α-Aminohelicin Hydrochloride.*

The removal of the acetyl groups from triacetyl-α-aminohelicin was complete on boiling in methyl alcohol containing 2 per cent. of hydrogen chloride for ninety minutes. During this process the specific rotation diminished from +192° to +13·7°. The product was isolated in the form of the hydrochloride in the usual manner, and was crystallised from ethyl alcohol containing a little ether.

Found: C=48·56; H=5·77; Cl=11·94.

$C_6H_{12}O_4N{\cdot}O{\cdot}C_6H_4{\cdot}CHO,HCl$ requires C=48·81; H=5·68; Cl=11·10 per cent.

*α-Aminohelicin hydrochloride* crystallises in prismatic needles, which decompose at 180° (corr.). The solubilities resemble those of the other aminoglucoside salts, but the compound is unique with respect to the ease with which it is hydrolysed. The specific rotation in water was −8·97° (without mutarotation), but this value is liable to correction, as the specimen appeared to contain a trace of glucosamine hydrochloride.

### *α-Aminosalicin Hydrochloride.*

A solution of dry saligenin (3 mols.) in anhydrous ether was added to finely-powdered bromotriacetylglucosamine hydrobromide (1 mol.), the mixture shaken for several hours, and put aside for one day. The ethereal layer, which was strongly acid, was then decanted, the solid residue washed with ether, and the treatment with saligenin repeated. The mixture was in this case boiled for five hours. After filtration, the solid residue was washed with ether and extracted with cold methyl alcohol. The solution thus obtained on evaporation to dryness gave a syrupy residue consisting of a mixture of the salts of the partly acetylated derivatives of α-aminosalicin. This was hydrolysed in the usual manner in methyl-alcoholic solution. During this change the solution became very dark, but the colour disappeared on neutralisation and subsequent treatment with animal charcoal. The crude salt was crystallised from methyl alcohol, and amounted to 20 per cent. of the weight of the bromo-compound originally used.

Found: C=48·20; H=6·36; Cl=11·11.

$C_6H_{12}O_4N\cdot O\cdot C_6H_4\cdot CH_2\cdot OH,HCl$ requires C=48·51; H=6·27; Cl=11·02 per cent.

*α-Aminosalicin hydrochloride* crystallises in colourless prisms, which decompose at 179° (corr.). The compound shows the usual glucosidic reaction with Fehling's solution, and is hydrolysed slowly on heating with 5 per cent. aqueous hydrogen chloride. The specific rotation in water ($c=3·606$) was −18·99°, and no mutarotation was detected. No colour reaction was given by ferric chloride solution, and thus the coupling of the glucosamine and saligenin residues must take place through the phenolic group.

### *α-Aminomorphineglucoside.*

In all the condensation reactions involving bromotriacetylglucosamine in which morphine was employed to remove hydrogen bromide, a small proportion of the base reacted with the bromo-compound. This was notably the case in the preparation of the methyl- and ethyl-aminoglucosides, where the morphine was used in solution. The essential product of this side-reaction is an acetylated aminoglucoside of morphine, which is found in the mother liquors after recrystallisation of the crude triacetyl-α-amino-alkylglucoside salts.

The material thus collected in the course of experiments involving the decomposition of 30 grams of the bromo-compound was hydrolysed in the usual manner by boiling for three hours in methyl alcohol containing 2 per cent. of hydrogen chloride. The liquid was then neutralised with silver carbonate, decolorised with charcoal, and concentrated to a syrup. The residue crystallised on keeping, and, after draining on porous porcelain, the crystals were purified by solution in methyl alcohol and fractional precipitation with ether.

Found: C=61·77; H=6·92.

$C_6H_{12}O_4N\cdot O\cdot C_{17}H_{18}O_2N$ requires C=61·84; H=6·78 per cent.

*α-Aminomorphineglucoside* crystallises in needles, which become brown at 160° and decompose at 248°. The compound has no action on Fehling's solution, but is very easily hydrolysed to give morphine and glucosamine salts. The specific rotation in methyl-alcoholic solution ($c=1$) was −113·5°. The properties of the compound showed that in its formation the reducing group of the sugar residue is coupled to the alkaloid through condensation with a hydroxyl group. This was confirmed by the fact that the base gave a glucosidic *dihydrochloride*. This crystallised in diamond-shaped plates, which decomposed at 204° (corr.).

Found: Cl = 13·53.

$C_6H_{12}O_4N{\cdot}O{\cdot}C_{17}H_{18}O_2N,2HCl$ requires Cl = 13·65 per cent.

The authors gratefully acknowledge a research grant received from the Carnegie Trust in aid of the above investigation.

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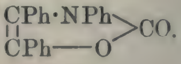
# IX.—*The Condensation of α-Keto-β-anilino-α-phenylethane and its Homologues with Carbonyl Chloride, Phenylcarbimide, and Phenylthiocarbimide.*

By HAMILTON McCOMBIE and HAROLD ARCHIBALD SCARBOROUGH.

IT has been shown by McCombie and Parkes (T., 1912, **101**, 1991) that dihydro-oxazolones can be obtained from α-keto-β-anilino-αβ-diphenylethane by two methods, namely, (i) the ketone was converted into its carbethoxy-derivative (I), which on treatment with potassium hydroxide in alcoholic solution lost the elements of alcohol with the formation of 3:4:5-triphenyl-2:3-dihydro-2-oxazolone (II); (ii) by the direct action of carbonyl chloride in toluene solution on the keto-compound, in the presence of pyridine, the same dihydro-oxazolone was produced:

$COPh{\cdot}CHPh{\cdot}NPh{\cdot}CO_2Et$

(I.)



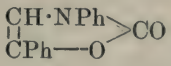
$$\left.\begin{array}{l}\mathrm{CPh{\cdot}NPh}\\ \|\\ \mathrm{CPh{-\!-}O}\end{array}\right>\mathrm{CO.}$$

(II.)

Attempts have now been made to extend this reaction to the preparation of dihydro-oxazolones containing one phenyl group less than the compounds described by McCombie and Parkes. The starting point for this work was α-keto-β-anilino-α-phenylethane (III), which is easily prepared from ω-bromoacetophenone by condensation with aniline. Attempts to prepare dihydro-oxazolones from this compound through the carbethoxy-derivative failed, as all attempts to prepare the latter yielded only the unchanged ketone. Success, however, attended the efforts when the second method of synthesis was employed. α-Keto-β-anilino-α-phenylethane, in the presence of pyridine, when condensed with carbonyl chloride in toluene solution, yielded 3:5-diphenyl-2:3-dihydro-2-oxazolone (IV) in almost quantitative yields:

$\mathrm{COPh\cdot CH_2\cdot NHPh}$

(III.)



$$\left.\begin{array}{l}\mathrm{CH\cdot NPh}\\ \|\\ \mathrm{CPh{-\!-}O}\end{array}\right>\mathrm{CO}$$

(IV.)

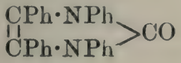
By similar condensations the corresponding *o*-, *m*-, and *p*-tolyl and β-naphthyl derivatives were obtained, these substituents being in each case attached to the nitrogen atom. The α-naphthyl derivative could not be prepared, but some of the substance was formed, and floated in the toluene layer, but could not be isolated and recrystallised.

These dihydro-oxazolones are very stable, the presence of the double bond did not lead to the addition of bromine, and the hydrogen atom in position 4 could not be substituted by bromine. The basicity of these compounds is so slight that no hydrochloride or picrate could be isolated.

Compounds similar to the sulphinazoles described by McCombie and Parkes (*loc. cit.*) might have been expected to arise from these ketones by condensation with thionyl chloride instead of carbonyl chloride. With α-keto-β-anilino-α-phenylethane and thionyl chloride, however, no change took place, the compound being recovered unchanged. With the analogous *p*-toluidine and β-naphthyl compounds a black, tarry mass was obtained, from which no crystalline product could be isolated; thus, thionyl chloride appears incapable of forming ring compounds with this series of ketones.

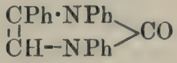
Brazier and McCombie (T., 1912, **101**, 2352) have shown that α-keto-β-anilino-αβ-diphenylethane and its homologues can be converted into ring compounds of the type 1:3:4:5-tetraphenyl-2:3-dihydro-2-glyoxalone (V) by condensation with phenylcarbimide. This synthesis has now been extended to include a series of dihydroglyoxalones having one phenyl group less.

Thus when phenylcarbimide was condensed with α-keto-β-anilino-α-phenylethane (III) there resulted 1:3:4-triphenyl-2:3-dihydro-2-glyoxalone (VI):



$$\left.\begin{array}{l}\mathrm{CPh\cdot NPh}\\ \|\\ \mathrm{CPh\cdot NPh}\end{array}\right>\mathrm{CO}$$

(V.)



$$\left.\begin{array}{l}\mathrm{CPh\cdot NPh}\\ \|\\ \mathrm{CH{-\!-}NPh}\end{array}\right>\mathrm{CO}$$

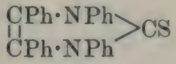
(VI.)

By similar condensations the homologous tolyl and β-naphthyl derivatives were obtained. The α-naphthyl derivative could not be isolated; an olive-green mass was formed, which could not be recrystallised.

These glyoxalones are stable compounds, and their basicity is of such an order as to give rise to picrates but no hydrochlorides. *o*-Tolylglyoxalone did not form a picrate which could be isolated, but the evidence seems to show that one is formed in hot glacial acetic acid solution.

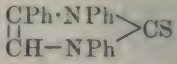
Brazier and McCombie (*loc. cit.*) found that two series of picrates were formed by the glyoxalones which they described, the series depending on the group attached to the nitrogen atom in position 3, and that the colour varied with the composition. Only one series of picrates was formed with these new glyoxalones, in which one molecule of the acid was combined with one molecule of the base, and the colours of the picrates varied between deep orange and red.

It has been shown by Brazier and McCombie (*loc. cit.*) that phenylthiocarbimide condenses with α-keto-β-anilino-αβ-diphenylethane to give 1:3:4:5-tetraphenyl-2:3-dihydro-2-glyoxalthione (VII). This condensation has been extended so as to give a series of dihydroglyoxalthiones containing one phenyl group less; thus, when phenylthiocarbimide reacted with α-keto-β-anilino-α-phenylethane we obtained 1:3:4-triphenyl-2:3-dihydro-2-glyoxalthione (VIII):



$$\left.\begin{array}{l}\mathrm{CPh{\cdot}NPh}\\ \|\\ \mathrm{CPh{\cdot}NPh}\end{array}\right>\mathrm{CS}$$

(VII.)



$$\left.\begin{array}{l}\mathrm{CPh{\cdot}NPh}\\ \|\\ \mathrm{CH{-}NPh}\end{array}\right>\mathrm{CS}$$

(VIII.)

By a similar series of condensations, the analogous *o*-, *m*-, and *p*-tolyl compounds were obtained. The α- and β-naphthyl compounds could not be isolated, as all attempts at crystallisation of the α-naphthyl derivative resulted in a viscid, syrupy liquid, and the β-naphthyl derivative gave a white, crystalline substance melting at 166—167°, and having a nitrogen content of 7·30 per cent.

## Experimental.

### 3:5-*Diphenyl*-2:3-*dihydro*-2-*oxazolone* (IV).

This compound was prepared by dissolving 2·1 grams of α-keto-β-anilino-α-phenylethane in 10 grams of pyridine, and adding 10 grams of a toluene solution of carbonyl chloride (20 per cent.). The mixture was cooled in ice, and, after eighteen hours, was poured into dilute hydrochloric acid to remove the pyridine. The oxazolone was precipitated in the toluene layer as a brown, flocculent mass, which was separated by filtration, decolorised by boiling with animal charcoal, and recrystallised three times from toluene, when it melted at 167—168°. The yield was nearly theoretical:

0·1500 gave 0·4180 $CO_2$ and 0·0627 $H_2O$. C = 76·00; H = 4·65.
0·1500 „ 7·9 c.c. $N_2$ at 15·5° and 725·3 mm. N = 5·83.
$C_{15}H_{11}O_2N$ requires C = 75·97; H = 4·64; N = 5·91 per cent.

3 : 5-*Diphenyl*-2 : 3-*dihydro-2-oxazolone* crystallises in white, glistening needles, which are soluble in glacial acetic acid or alcohol in the cold, and moderately so in most organic solvents on warming.

No salt with picric acid could be prepared in glacial acetic acid solution, or by fusing with the acid alone. Bromination of the compound in chloroform solution could not be effected. No hydrochloride could be isolated in an alcoholic or a glacial acetic acid solution.

### 5-*Phenyl*-3-o-*tolyl*-2 : 3-*dihydro-2-oxazolone*, $C_{16}H_{13}O_2N$.

This compound was prepared in the same manner, except that it was allowed to remain for three days before the condensation was complete. The yield was 60 per cent. of that required by theory, and the substance melted at 124—125°:

0·2000 gave 0·5602 $CO_2$ and 0·0937 $H_2O$. C = 76·4; H = 5·20.
0·2000 „ 9·95 c.c. $N_2$ at 21° and 752 mm. N = 5·57.
$C_{16}H_{13}O_2N$ requires C = 76·4; H = 5·18; N = 5·58 per cent.

### α-*Keto*-β-m-*toluidino*-α-*phenylethane*, $C_{15}H_{15}ON$.

This substance was prepared by dissolving 10 grams of ω-bromoacetophenone in 40 grams of alcohol, and then adding 11 grams of *m*-toluidine. After remaining at room temperature for thirty minutes, the liquid changed to a yellow, almost solid mass. This solid was separated and recrystallised three times from alcohol, when it melted at 113—114°. The compound crystallises in small, lemon-yellow needles, which are soluble in all common organic solvents. The yield was theoretical:

0·2000 gave 0·5866 $CO_2$ and 0·1216 $H_2O$. C = 79·99; H = 6·70.
$C_{15}H_{15}ON$ requires C = 80·0; H = 6·66 per cent.

The analogous aniline and *o*-toluidine compounds have been prepared by Bischler (*Ber.*, 1892, **25**, 2860), the α- and β-naphthylamine derivatives by Kunckell (*Ber.*, 1897, **30**, 575), and the *p*-toluidine compound by Lellmann and Donner (*Ber.*, 1890, **23**, 167). They were prepared more easily by the authors in the manner described for α-keto-β-*m*-toluidino-α-phenylethane.

### 5-*Phenyl*-3-m-*tolyl*-2 : 3-*dihydro-2-oxazolone*, $C_{16}H_{13}O_2N$.

This oxazolone is soluble to a greater extent in toluene, and an increased yield is obtained by evaporating, in a brisk draught, the toluene layer which is formed on pouring the condensation mixture into dilute acid. The crystals are needle-shaped, and unite to form clotted masses, which melt at 84—85°:

The yield was 60 per cent. of the theoretical:

0·2000 gave 0·5594 $CO_2$ and 0·0950 $H_2O$. C=76·29; H=5·27.

$C_{16}H_{13}O_2N$ requires C=76·40; H=5·18 per cent.

### 5-*Phenyl*-3-p-*tolyl*-2:3-*dihydro*-2-*oxazolone*, $C_{16}H_{13}O_2N$.

This compound crystallises from toluene in long needles, which unite to form clotted masses, and melts at 173—174°:

0·2000 gave 0·5608 $CO_2$ and 0·0950 $H_2O$. C=76·43; H=5·27.

0·2000 „ 10·05 c.c. $N_2$ at 21·5° and 748 mm. N=5·59.

$C_{16}H_{13}O_2N$ requires C=76·40; H=5·18; N=5·58 per cent.

### 5-*Phenyl*-3-β-*naphthyl*-2:3-*dihydro*-2-*oxazolone*, $C_{19}H_{13}O_2N$.

This compound crystallises from toluene in shining needles melting at 193—194°:

0·2000 gave 0·5870 $CO_2$ and 0·0822. C=80·04; H=4·57.

0·2000 „ 8·85 c.c. $N_2$ at 16° and 739·5 mm. N=4·92.

$C_{19}H_{13}O_2N$ requires C=80·00; H=4·53; N=4·88 per cent.

### 1:3:4-*Triphenyl*-2:3-*dihydro*-2-*glyoxalone* (VI).

This compound is prepared by heating on a water-bath for three hours a mixture of α-keto-β-anilino-α-phenylethane (2·1 grams) and phenylcarbimide (1·5 grams). A clear solution is first formed, which gradually solidifies. On further heating water is eliminated and a white mass obtained. This mass is dissolved in alcohol, and 1 c.c. of concentrated hydrochloric acid is added, and the solution heated under reflux for three hours. On cooling, the glyoxalone separates in clotted, white masses, which after five recrystallisations melted at 164—165° The substance can be equally well recrystallised from toluene, and is soluble on warming in all common organic solvents. The yield was 2·5 grams:

0·2010 gave 0·5958 $CO_2$ and 0·0936 $H_2O$. C=80·84; H=5·17.

0·1518 „ 12·5 c.c. $N_2$ at 21° and 735 mm. N=9·01.

$C_{21}H_{16}ON_2$ requires C=80·76; H=5·12; N=8·97 per cent.

The *picrate* was prepared in a boiling acetic acid solution, from which it crystallises in deep crimson needles melting at 130—131°. This salt is readily decomposed by boiling with water, alcohol, or alkali, with regeneration of the glyoxalone:

0·2094 gave 0·4594 $CO_2$ and 0·0676 $H_2O$. C=59·84; H=3·58.

$C_{21}H_{16}ON_2,C_6H_3O_7N_3$ requires C=59·88; H=3·51 per cent.

### 3:4-*Diphenyl*-1-o-*tolyl*-2:3-*dihydro-2-glyoxalone*, $C_{22}H_{18}ON_2$.

This compound crystallises from alcohol in small, glistening needles, which melt at 159—160°:

0·2099 gave 0·6251 $CO_2$ and 0·1066 $H_2O$. C=81·15; H=5·64.
$C_{22}H_{18}ON_2$ requires C=80·98; H=5·52 per cent.

No picrate of this glyoxalone could be isolated, either by fusing with picric acid or by boiling with picric acid in acetic acid solution, although the mixture assumed a deep red colour, similar to that exhibited by the other glyoxalones.

### 3:4-*Diphenyl*-1-m-*tolyl*-2:3-*dihydro-2-glyoxalone*, $C_{22}H_{18}ON_2$.

This substance crystallises from alcohol in fine, white needles, which unite to form clotted masses, and melt at 135—136°:

0·2152 gave 0·6384 $CO_2$ and 0·1101 $H_2O$. C=80·90; H=5·68.
$C_{22}H_{18}ON_2$ requires C=80·98; H=5·52 per cent.

The *picrate* crystallises from glacial acetic acid in deep scarlet, glistening needles, which melt at 126—127°:

0·2061 gave 0·4563 $CO_2$ and 0·0747 $H_2O$. C=60·39; H=4·02.
$C_{22}H_{18}ON_2,C_6H_3O_7N_3$ requires C=60·53; H=4·02 per cent.

### 3:4-*Diphenyl*-1-p-*tolyl*-2:3-*dihydro-2-glyoxalone*, $C_{22}H_{12}ON_2$.

This substance crystallises from alcohol in fine, small needles, which melt at 165—166°:

0·2000 gave 0·5924 $CO_2$ and 0·1018 $H_2O$. C=80·78; H=5·65.
0·3000 „ 23·4 c.c. $N_2$ at 22° and 748·5 mm. N=8·65.
$C_{22}H_{18}ON_2$ requires C=80·98; H=5·52; N=8·59 per cent.

The *picrate* separates from glacial acetic acid in deep red, glistening needles, which melt at 136—137°:

0·2086 gave 0·4638 $CO_2$ and 0·0729 $H_2O$. C=60·61; H=3·88.
$C_{22}H_{18}ON_2,C_6H_3O_7N_3$ requires C=60·53; H=3·78 per cent.

### *Phenyl-β-naphthylbenzoylmethylcarbamide*,
### $CH_2Bz\cdot N(C_{10}H_7)\cdot CO\cdot NHPh$.

If a mixture of α-keto-β-2-naphthylamino-α-phenylethane (2·6 grams) and phenylcarbimide (1·5 grams) is heated very gently on a water-bath, a white product is obtained. This is kept for a short time in contact with alcohol, and is then recrystallised from toluene, when it melts at 167—168°:

0·1390 gave 0·4026 $CO_2$ and 0·0652 $H_2O$. C=78·97; H=5·21.
$C_{25}H_{20}O_2N_2$ requires C=78·93; H=5·26 per cent.

This compound, on boiling with alcohol, loses water, and is converted into the glyoxalone.

### 3 : 4-*Diphenyl*-1-β-*naphthyl*-2 : 3-*dihydro*-2-*glyoxalone*, $C_{25}H_{18}ON_2$.

This substance crystallises from alcohol or toluene in glistening needles, which melt at 175—176° :

0·2000 gave 0·6074 $CO_2$ and 0·0903 $H_2O$. C = 82·83 ; H = 5·02.
$C_{25}H_{18}ON_2$ requires C = 82·87 ; H = 4·97 per cent.

The *picrate* crystallises from glacial acetic acid in orange-brown needles, which melt at 167—168° :

0·2002 gave 0·4620 $CO_2$ and 0·0664 $H_2O$. C = 62·96 ; H = 3·70.
$C_{25}H_{18}ON_2,C_6H_3O_7N_3$ requires C = 62·93 ; H = 3·53 per cent.

### 1 : 3 : 4-*Triphenyl*-2 : 3-*dihydro*-2-*glyoxalthione* (VIII).

This substance was prepared by heating 2·1 grams of α-keto-β-anilino-α-phenylethane and 1·7 grams of phenylthiocarbimide in an oil-bath at 130—140° for three to four hours. The product was then crystallised from toluene, when it separated in small, glistening needles, melting at 170—171°. The needles are not quite white even after seven recrystallisations, but have a slight yellow tinge. The compound can be recrystallised from alcohol, and is soluble in most organic solvents. The yield is about 30—40 per cent. of the theoretical :

0·2066 gave 0·5810 $CO_2$ and 0·0893 $H_2O$. C = 76·70 ; H = 4·80.
0·1525 „ 11·6 c.c. $N_2$ at 15° and 744·3 mm. N = 8·68.
0·2817 „ 0·2019 $BaSO_4$. S = 9·84.
$C_{21}H_{16}N_2S$ requires C = 76·82 ; H = 4·87 ; N = 8·57 ; S = 9·75 per cent.

### 3 : 4-*Diphenyl*-1-o-*tolyl*-2 : 3-*dihydro*-2-*glyoxalthione*, $C_{22}H_{18}N_2S$.

This compound crystallises from toluene in small, glistening needles, melting at 165—166° :

0·1650 gave 0·4680 $CO_2$ and 0·0786 $H_2O$. C = 77·33 ; H = 5·29.
$C_{22}H_{18}N_2S$ requires C = 77·20 ; H = 5·29 per cent.

### 3 : 4-*Diphenyl*-1-m-*tolyl*-2 : 3-*dihydro*-2-*glyoxalthione*, $C_{22}H_{18}N_2S$.

This substance crystallises from toluene in small, white needles, melting at 168—169° :

0·1738 gave 0·4920 $CO_2$ and 0·0836 $H_2O$. C = 77·29 ; H = 5·3.
$C_{22}H_{18}N_2S$ requires C = 77·20 ; H = 5·26 per cent.

### 3:4-*Diphenyl*-1-p-*tolyl*-2:3-*dihydro*-2-*glyoxalthione*, $C_{22}H_{18}N_2S$.

When recrystallised from toluene, this substance separates in long, white needles, which unite to form clotted masses melting at 192—193°:

0·1533 gave 0·4355 $CO_2$ and 0·0710 $H_2O$. C=77·46; H=5·15.

$C_{22}H_{18}N_2S$ requires C=77·20; H=5·26 per cent.

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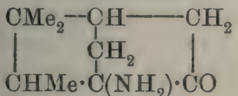
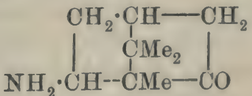
## X.—*Studies in the Camphane Series. Part XXXIII.* *Orientation of Tiemann's* iso*Aminocamphor.*

By MARTIN ONSLOW FORSTER and HUBERT ARTHUR HARRY HOWARD.

IN addition to ordinary aminocamphor, obtainable by reducing α-nitrocamphor (Schiff, *Ber.*, 1880, **13**, 1404) and *iso*nitrosocamphor (Claisen and Manasse, *Annalen*, 1893, **274**, 90; also Duden and Pritzkow, *Ber.*, 1899, **32**, 1539), and therefore regarded as having the amino-group in the α-position, there exists an isomeric substance discovered by Tiemann (*Ber.*, 1895, **28**, 1082; 1897, **30**, 321), known as *iso*aminocamphor, which has not been since investigated, and in which the position of the substituent has not been determined. It is true that the discoverer ascribed to it a constitutional formula (I) based on the ideas he then entertained concerning the structure of camphor, but a general survey of the evidence regarded in the light of Bredt's formula for camphor led us to consider the probability of its belonging to the β-series of derivatives, and having accordingly the constitution represented by formula (II):



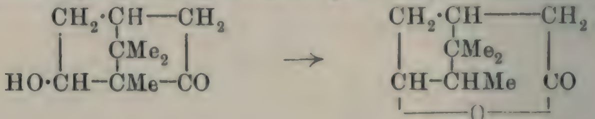
(I.)



(II.)

In the present paper we describe experiments which confirm this view.

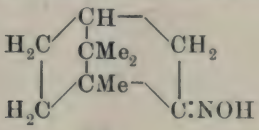
The β-series has hitherto comprised only three mono-substituted derivatives of camphor. The bromo-compound was obtained simultaneously from two sources, namely, the bromide of Reychler's camphorsulphonic acid (Armstrong and Lowry, P., 1901, **17**, 244) and from hydroxycamphene on treatment with bromine (Forster, *ibid.*, 245). β-Chlorocamphor arises from hydroxycamphene and chlorine (T., 1902, **81**, 264), whilst the sulphonic acid just mentioned is the third member of the series (Armstrong and Lowry, *ibid.*, 1469). To this group must now be added Tiemann's *iso*aminocamphor (II) and a new, highly unstable hydroxycamphor (III), which rapidly changes into dihydrocampholenolactone (IV):



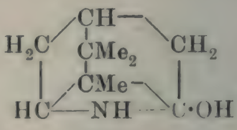
(III.) (IV.)

Our reasons for making this classification may be summarised in the statement that *iso*aminocamphor can be produced directly from β-bromocamphor by the action of alcoholic ammonia, whilst indirectly the halogen derivative can be regenerated from the first-named substance. We therefore use the expression β-aminocamphor in place of *iso*aminocamphor.

The production of β-aminocamphor by Tiemann's process, namely, action of hydriodic acid on camphoroxime (V) must depend on the principle invoked to explain the formation of β-bromocamphor and β-chlorocamphor by the action of halogens on hydroxycamphene (T., 1902, **81**, 268). Owing to the strains set up in the camphor molecule it is reasonable to suppose that the β-position approximates in space to the ketonic carbon, thereby facilitating the production of an intermediate compound (VI), which would be a *cyclo*imino-derivative of hydroxycamphane:

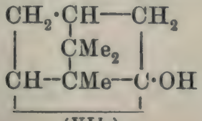


(V.)

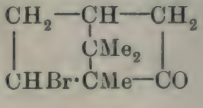


(VI.)

A substance of this structure might be expected to pass readily into the isomeric β-aminocamphor (II), or to be produced easily from it, and we find, in fact, that when the solid hydrochloride of the base in question is heated under diminished pressure, there distils a compound, $C_{10}H_{17}ON$, melting at 71°, and slowly changing at the ordinary temperature into the isomeric β-campholenamide,



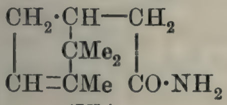
(VII.)



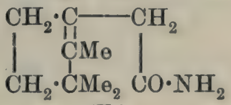
(VIII.)

melting at 52°. Moreover, when this material (m. p. 71°) is subjected to the treatment which converted hydroxycamphene (VII) into β-bromocamphor (VIII), the latter substance is likewise produced.

Similarly, by the action of chlorine, the compound melting at 71°, and believed to have the constitution (VI), is converted into β-chlorocamphor; moreover, like camphoroxime itself, it is transformed by hydriodic acid into β-aminocamphor, accompanied by a small proportion of campholenonitrile, and we therefore suggest that the conversion of camphoroxime into Tiemann's base depends on the intermediate formation of the *cyclo*iminohydroxycamphane (VI). Furthermore, we have found that an attempt to prepare a benzenesulphonyl derivative transforms β-aminocamphor into α-campholenamide (IX), although an aqueous solution of the hydrochloride yields β-campholenamide (X) when gently warmed:



(IX.)



(X.)

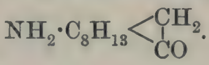
This is the only case in which an α-campholenic derivative has been produced directly from β-aminocamphor, and is therefore comparable with the direct formation of α-campholenic acid by the action of alcoholic alkali on β-bromocamphor (VIII), thus adding support to our contention that the amino-group occupies the β-position.

Tiemann found that the amino-group in β-aminocamphor is attached so loosely that treatment with hydroxylamine converts it into two isomeric oximes of a hydroxycamphor, which he was not able to isolate owing to the readiness with which it passes into dihydrocampholenolactone. We find that semicarbazide also gives two isomeric substances, from which the original amino-group has disappeared, giving place to hydroxyl; the α-semicarbazone melts at 162°, whilst the β-modification melts at 145°, thereupon changing into the less fusible isomeride. Although dilute hydrochloric acid transforms the α-semicarbazone into dihydrocampholenolactone (IV), a distinctly different substance can be produced by hydrolysis with aqueous oxalic acid; this we believe to be the β-hydroxycamphor (III) which Tiemann failed to isolate, because it yields the hydroxycamphoroximes which Tiemann obtained from β-aminocamphor, and changes with hot water into dihydrocampholenolactone (IV).

In connexion with the question of optical activity, it is noteworthy that although camphoroxime and the β-halogen derivatives of camphor are active, β-aminocamphor, as stated by Tiemann, together with its *p*-toluenesulphonamide and the semicarbazone of β-hydroxycamphor, are optically inactive. A similar case has been recorded by W. H. Perkin (P., 1910, **26**, 97) during the synthesis of sylvestrene, when *d*-1-methyl-$\Delta^1$-*cyclo*hexene-3-carboxylic acid ($[\alpha]_D$ 66°) in the form of its ethyl ester is converted by the Grignard agent into *d*-dihydrocarvestrenol (almost inactive), from which hydrogen chloride produces sylvestrene dihydrochloride ($[\alpha]_D$ 22·6°); the hydrocarbon to which this gives rise is also active, having $[\alpha]_D$ 66·3°.

## EXPERIMENTAL.

### *β-Aminocamphor, the* iso*Aminocamphor of Tiemann,*



$$\mathrm{NH_2{\cdot}C_8H_{13}}<\begin{matrix}\mathrm{CH_2}\\ | \\ \mathrm{CO}\end{matrix}.$$

The preparation of the base described by Tiemann depends on the transformation of camphoroxime by either sulphuric acid (1:1) or hydriodic acid (D 1·96). We find that the latter agent is more convenient if camphoroxime itself is employed, yields of 40 per cent. being usually obtained, but as the remaining product is campholenonitrile, it is more economical to use this material as a source of the base, into which it is converted almost quantitatively by hydriodic acid of the concentration indicated. Since campholenonitrile is readily obtainable from camphoroxime by the action of hydrochloric or sulphuric acid, waste of the more costly hydriodic acid may be reduced to a minimum.

*Conversion into α-Campholenamide.*—On attempting to prepare the benzenesulphonyl derivative of β-aminocamphor by agitating an alkaline solution with the calculated amount of benzenesulphonyl chloride, colourless crystals melting at 130° were produced, but the product did not contain sulphur, and was found to consist of α-campholenamide.

*The Toluenesulphonyl Derivative.*—Six grams of β-aminocamphor hydriodide dissolved in water and rendered alkaline gave an ethereal solution of the base, which, when dried with potassium carbonate and mixed with 1·9 grams of *p*-toluenesulphonyl chloride, yielded a precipitate of β-aminocamphor hydrochloride during twenty-four hours, whilst the filtrate deposited crystals on evaporation; recrystallisation from benzene diluted with petroleum gave pale yellow needles melting and decomposing at 115°:

0·3480 gave 15·4 c.c. $N_2$ at 17° and 750 mm. N=4·66.

$C_{17}H_{23}O_3NS$ requires N=4·36 per cent.

p-*Toluenesulphonyl-β-aminocamphor* is optically inactive. It is completely hydrolysed by warm alkali to β-aminocamphor and *p*-toluenesulphonic acid, but in three hours it is converted by boiling water into dihydrocampholenolactone.

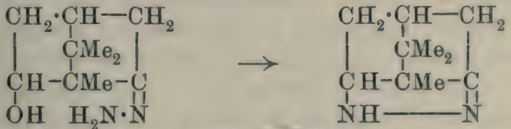
*Action of Hydrazine Acetate.*—β-Aminocamphor hydriodide, when mixed with hydrazine sulphate and sodium acetate in aqueous solution, deposited during twelve hours a brown, viscous mass, from which dihydrocampholenolactone could be isolated as a result of dissolving in alcohol and diluting with water; the mother liquor, when cooled with ice, gave a crystalline product, which, on recrystallisation from dilute alcohol, reduced ammoniacal silver oxide and mercury acetamide when fresh. In the desiccator, however, this property gradually disappeared, and the melting point rose, with lapse of several weeks, to 178°:

0·1096 gave 17 c.c. $N_2$ at 26° and 745 mm. N = 17·35.

$C_{10}H_{18}ON_2$ requires N = 15·38 per cent.

$C_{10}H_{16}N_2$ „ N = 17·08 „ „

It would appear, therefore, that the first action of hydrazine is to produce the hydrazone of β-hydroxycamphor, which then undergoes internal condensation, as follows:



Unlike β-aminocamphor, the substance is optically active, a solution containing 0·2680 gram in chloroform, made up to 25 c.c., giving $\alpha_D$ 40′ in a 2-dcm. tube, whence $[\alpha]_D$ 31·1°.

### *Conversion of β-Bromocamphor into β-Aminocamphor.*

One gram of the halogen derivative was heated with 20 c.c. of alcoholic ammonia during three hours in a sealed tube at 170°; 0·5 gram of benzaldehyde was then added to the product, which, after forty-eight hours, was diluted with water. The benzylidene derivative of β-aminocamphor separated, melting at 98° after recrystallisation from dilute alcohol. (Found, N = 5·40. $C_{17}H_{21}ON$ requires N = 5·49 per cent.)

In another experiment the liquid, after being heated in the sealed tube, was diluted with water and extracted with ether, this being shaken with dilute hydrochloric acid; on mixing the acid liquid with semicarbazide hydrochloride and sodium acetate, the semicarbazone of β-hydroxycamphor (see below) crystallised in the course of a few hours, melting at 162°. The ethereal liquid left a small quantity of dihydrocampholenimide (m. p. 108°) on evaporation.

### *Conversion of β-Aminocamphor into β-Bromocamphor.*

On heating 5 grams of β-aminocamphor hydrochloride under 30 mm. pressure, a colourless distillate was produced above 180°, solidifying in the receiver; recrystallisation from hot water gave colourless, felted needles, melting at 71°:

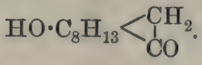
0·1200 gave 8·8 c.c. $N_2$ at 21° and 755 mm. N = 8·50.
$C_{10}H_{17}ON$ requires N = 8·44 per cent.

After several days in the desiccator the substance was found to melt at 52°, having changed into β-campholenamide; this was further identified by hydrolysis to β-campholenic acid, m. p. 51°. Production of β-campholenamide also followed an attempt to prepare a benzoyl derivative in pyridine, whilst α-campholenamide arose when the Schotten-Baumann process was pursued.

As already explained, the initial product of dry distillation (m. p. 71°) is to be regarded as a *cyclo*imino-derivative of hydroxycamphane (VI), and might therefore be convertible into β-bromocamphor under conditions which generated that substance from hydroxycamphene. One gram was accordingly dissolved in 10 c.c. of glacial acetic acid, to which 3 grams of anhydrous sodium acetate was added; 1 gram of bromine in 10 c.c. of glacial acetic acid was poured slowly into the cooled liquid, and was decolorised immediately. After fifteen minutes, dilution with water precipitated β-bromocamphor melting at 78°, and having $[\alpha]_D$ 16·2° in chloroform (4 per cent.). It is worth while to emphasise the fact that the product has the same rotatory power as a specimen from hydroxycamphene, because β-aminocamphor is stated by Tiemann to be optically inactive; this property must therefore be due to a fortuitous internal compensation, and not to racemisation of the camphor molecule by hydriodic acid.

On treating the *cyclo*imino-compound (m. p. 71°) with chlorine dissolved in glacial acetic acid in presence of sodium acetate, water precipitated β-chlorocamphor, which, after recrystallisation from dilute alcohol, was found to be identical in melting point and specific rotatory power with the substance obtained in the same way from hydroxycamphene.

### *β-Hydroxycamphor*,



$HO\cdot C_8H_{13}<\begin{matrix}CH_2\\ |\\ CO\end{matrix}$.

Three grams of β-aminocamphor hydriodide and 3 grams of sodium acetate having been dissolved in 30 c.c. of water, 1 gram of semicarbazide hydrochloride in 5 c.c. of water was added to the filtered liquid, the crystals separating during twelve hours being dried in the desiccator before treatment with a small quantity of hot petroleum (b. p. 60—80°), which dissolved the labile β-semicarbazone, leaving the insoluble, stable isomeride. This was recrystallised from benzene diluted with petroleum:

0·0941 gave 15·1 c.c. $N_2$ at 22° and 750 mm. N=18·39.

$C_{11}H_{19}O_2N_3$ requires N=18·67 per cent.

The *α-semicarbazone* of β-hydroxycamphor forms lustrous plates melting at 162°; it dissolves readily in benzene or alcohol, and is optically inactive.

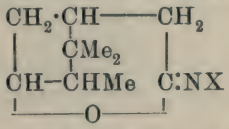
The *β-semicarbazone* separated as a snow-white, crystalline powder on allowing the filtrate from the initial extraction to evaporate:

0·0996 gave 17·0 c.c. $N_2$ at 26° and 745 mm. N=19·09.

$C_{11}H_{19}O_2N_3$ requires N=18·67 per cent.

This modification melted at 145°, above which temperature the fused material solidified; after recrystallisation from benzene diluted with petroleum, it melted at 162°, and did not depress the melting point of the α-semicarbazone.

*Hydrolysis of the Semicarbazone.*—When the α-semicarbazone was treated with warm, dilute hydrochloric acid, the oily product had the odour of dihydrocampholenolactone, and was ultimately identified as that substance (m. p. 30°). On heating 5 grams of the semicarbazone with 5 grams of oxalic acid in 25 c.c. of water, however, there separated an oil with the odour of borneol; on removing this with ether, and heating an alcoholic solution with hydroxylamine acetate, rapid precipitation of the colourless oxime (m. p. 165°) obtained by Tiemann from β-aminocamphor itself (*Ber.*, 1897, **30**, 330) took place. Under similar conditions, dihydrocampholenolactone does not yield an oxime, thus excluding the constitution,

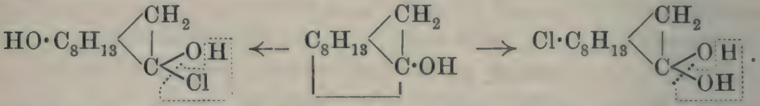


for the oximes and semicarbazones to which β-aminocamphor gives rise.

β-Hydroxycamphor is even more unstable than β-aminocamphor, being more closely comparable with β-dimethylaminocamphor; when heated with water during half-an-hour it is transformed into dihydrocampholenolactone. Tiemann remarks (*Ber.*, 1895, **28**, 2170) that on distilling dihydrocampholenolactone prepared by the spontaneous decomposition of aqueous β-aminocamphor hydrochloride at the ordinary temperature, the higher fractions have an odour more camphor-like than that of the lactone itself, and suggests that at elevated temperatures the lactone is transformed into the hydroxycamphor corresponding with the amino-derivative. He records also an attempt to produce this hydroxycamphor from β-aminocamphor hydrochloride and sodium nitrite, but this led only to dihydrocampholenolactone.

Having produced in the manner described above the substance which we believe to be β-hydroxycamphor, an attempt was made to convert this into β-chlorocamphor by the action of thionyl chloride in presence of dimethylaniline (compare Darzens, *Compt. rend.*, 1911, **152**, 1314); this was unsuccessful, however, the sole product consisting of dihydrocampholenolactone. Similarly, application of Darzens' process to the α-semicarbazone of β-hydroxycamphor in the hope of arriving at the semicarbazone of β-chlorocamphor, led to dihydrocampholenolactone. Furthermore, it has to be noted that an attempt to hydrolyse the α-semicarbazone of β-hydroxycamphor with aqueous benzaldehyde failed; benzylidenesemicarbazone was certainly produced, but the other product was dihydrocampholenolactone instead of β-hydroxycamphor.

Since hydroxycamphene gives β-chloro- and β-bromocamphor by the action of chlorine and of bromine, respectively, it seemed possible that hypochlorous acid might give rise to β-hydroxycamphor under similar conditions, although, of course, β-chlorocamphor is the alternative possibility:



The latter, in fact, is the direction taken, a specimen of β-chlorocamphor (m. p. 133°) being obtained. Hydrogen peroxide, which might also have yielded β-hydroxycamphor, left hydroxycamphene unchanged.

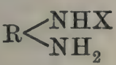
An abridged account of the results of this investigation was presented to the Eighth International Congress of Applied Chemistry, New York, 1912.

Royal College of Science, London.
South Kensington, S.W.

# XI.—*The Constitution of the ortho-Diazoimines. Part II. The* p-*Tolyl-β-naphthatriazoles.*

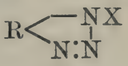
By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

THE uncertainty formerly existing in regard to the constitution of the diazoimino-compounds or *iso*triazoles produced by treating with nitrous acid the aromatic ortho-diamines and their mono-*N*-substituted derivatives (I) has been removed by the results of an investigation by one of us in conjunction with W. Godden, in which it was shown that the two benzenesulphonyl-1 : 2-naphthylenediamines give rise to isomeric *iso*triazoles (T., 1910, **97**, 1702), thereby demonstrating that the symmetric formula (III) for these diazo-derivatives advocated by Griess must be rejected in favour of the dissymmetric configuration (II) put forward by Kekulé:

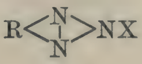

$R\Big\langle\begin{matrix}NHX\\NH_2\end{matrix}$

(I.)

$\longrightarrow$


$R\Big\langle\begin{matrix}-NX\\ \quad|\\N{:}N\end{matrix}$

(II.)


$R\Big\langle\begin{matrix}N\\|\\N\end{matrix}\Big\rangle NX$

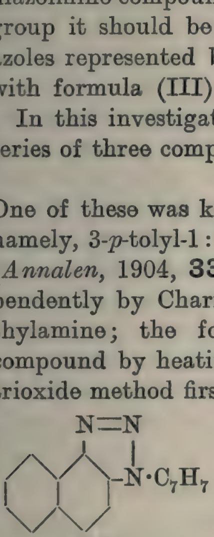
(III.)

If the constitution indicated by formula (II) is possessed by diazoimino-compounds in general, then when X is an aromatic group it should be possible to obtain three isomerides, two *iso*triazoles represented by this formula, and one triazole corresponding with formula (III).

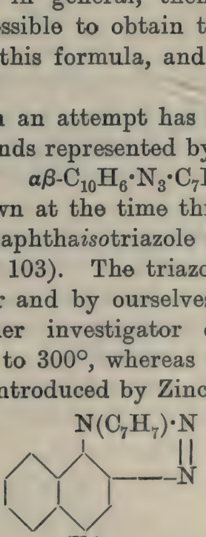
In this investigation an attempt has been made to complete the series of three compounds represented by the general formula

$$\alpha\beta\text{-}C_{10}H_6\cdot N_3\cdot C_7H_7.$$

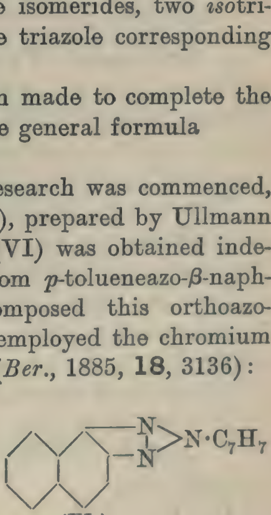
One of these was known at the time this research was commenced, namely, 3-*p*-tolyl-1 : 2-naphtha*iso*triazole (IV), prepared by Ullmann (*Annalen*, 1904, **332**, 103). The triazole (VI) was obtained independently by Charrier and by ourselves from *p*-tolueneazo-β-naphthylamine; the former investigator decomposed this orthoazo-compound by heating to 300°, whereas we employed the chromium trioxide method first introduced by Zincke (*Ber.*, 1885, **18**, 3136):



(IV.)



(V.)



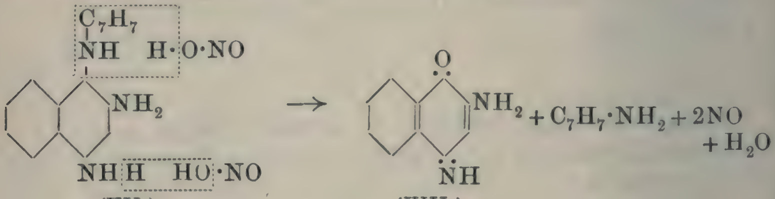
(VI.)

Many attempts have been made to obtain the third isomeride (V) from 1-p-*tolyl*-1 : 2 : 4-*triaminonaphthalene* (VII), a somewhat unstable base obtained by reducing 2 : 4-*dinitro*-1-p-*tolyl*-α-*naphthylamine*, but although various modifications of the diazo-reaction were employed the desired result was not obtained.

With nitrosyl sulphate in 80 per cent. sulphuric acid, followed by treatment with alcohol and copper powder, the triamine underwent condensation, yielding as the main product a complex nitroso-derivative (compare Zincke and Campbell, *Annalen*, 1889, **255**, 351), from which the *iso*triazole could not be prepared. A small amount of a by-product was isolated, which appeared to be an ethoxy-derivative of the required *iso*triazole.

The interaction of nitrous acid or the alkyl nitrites with the triamine and its salts, which takes a totally different course, is very remarkable, inasmuch as neither of the two amino-groups undergoes diazotisation, one being oxidised whilst the other remains unchanged.

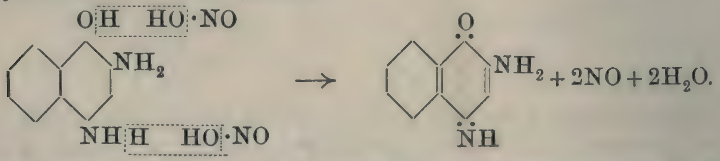
The first effect of nitrous acid on the triamine is one of oxidation, the products being 2-amino-1:4-naphthaquinoneimide (VIII) and *p*-toluidine, as indicated by the following equation:



(VII.) (VIII.)

In the presence of hydrochloric acid the quinoneimide is precipitated as its red, sparingly soluble hydrochloride, whereas the *p*-toluidine hydrochloride is diazotised by a further portion of the nitrous acid or alkyl nitrite, so that the filtrate gives an azo-compound with alkaline β-naphthol.

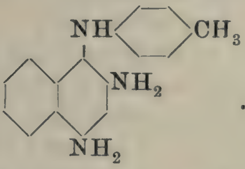
With the object of elucidating the foregoing changes a comparative experiment was made with 2:4-diamino-α-naphthol, when it was found that this substance also undergoes oxidation with nitrous acid or the alkyl nitrites, yielding the same product, 2-amino-1:4-naphthaquinoneimide. This method of preparing the substance is preferable to that in which ferric chloride is employed, and may prove to be of general application in the case of other aromatic polyamines and aminophenols:



The hydrochloride of 2-amino-1:4-naphthaquinoneimide is not diazotisable with sodium nitrite or the alkyl nitrites in aqueous, alcoholic, or glacial acetic acid solutions. Treatment with excess of nitrosyl sulphate in 80 per cent. sulphuric acid leads to decomposition with loss of a portion of the nitrogen, but there is no indication that any diazotisation occurs.

## EXPERIMENTAL.*

### 1-p-*Tolyl*-1:2:4-*triaminonaphthalene*,



1-Chloro-2:4-dinitronaphthalene, prepared by following Ullmann's directions (*Ber.*, 1908, **41**, 3932; D.R.-P. 199318), was the starting point in this investigation. Toluene-*p*-sulphonyl chloride (19 grams) recrystallised from light petroleum was added to a solution of 2:4-dinitro-α-naphthol (24 grams) dissolved in redistilled diethylaniline (30 grams), and the mixture heated on the water-bath for two to three hours. After extracting the product successively with *N*-hydrochloric acid, very dilute ammonia, and alcohol (the last solvent being used to remove tarry impurities), the residual 1-chloro-2:4-dinitronaphthalene (yield, 19 grams) melted at 140—141°, and was sufficiently pure for the next operation.

### 2:4-*Dinitro*-1-p-*tolyl*-α-*naphthylamine*, $C_{10}H_5(NO_2)_2{\cdot}NH{\cdot}C_7H_7$.

1-Chloro-2:4-dinitronaphthalene (10 grams), dissolved in dry xylene, was boiled for five hours with *p*-toluidine (8·4 grams); *p*-toluidine hydrochloride sublimed into the condenser, and, when diluted with alcohol, the solution yielded a copious, yellow precipitate, which was extracted with warm dilute alcohol to remove *p*-toluidine hydrochloride. The residue, which crystallised well from alcohol, glacial acetic acid, or xylene, separated in felted, yellow needles, and melted at 203—204°, the yield being about 12 grams:

0·1600 gave 18·0 c.c. $N_2$ at 13° and 745 mm. N=13·05.

$C_{17}H_{13}O_4N_3$ requires N=13·00 per cent.

2:4-Dinitro-1-*p*-tolyl-α-naphthylamine was also obtained by the simultaneous interaction of 2:4-dinitro-α-naphthol, *p*-toluidine, and toluene-*p*-sulphonyl chloride dissolved in dimethyl- or diethylaniline.

The dinitro-compound (1·5 grams) dissolved in 100 c.c. of alcohol was reduced by boiling with ammonium chloride (1 gram), zinc (4—5 grams), and a few drops of water. With the large excess of zinc the reduction proceeded fairly readily to a colourless solution with an intermediate dark red stage. The filtrate from the zinc oxy-compounds was diluted with cold water rendered slightly alkaline, the precipitated base was redissolved in *N*-hydrochloric acid, reprecipitated with cold dilute ammonia, stirred until granular, and dried on a porous tile:

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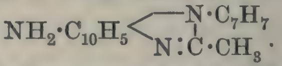
* The earlier experiments in this investigation were carried out by Mr. A. Bramley, B.Sc., A.R.C.Sc., for whose help we desire to express our best thanks.

0·2208 gave 30 c.c. $N_2$ at 13° and 766 mm. N = 16·17.

$C_{17}H_{17}N_3$ requires N = 15·96 per cent.

1-p-*Tolyl*-1:2:4-*triaminonaphthalene* is a very oxidisable base, especially in wet solvents. It resinified in air, dissolved in benzene with a certain amount of decomposition, and crystallised in fan-shaped aggregates of glistening, colourless, opaque needles. After two crystallisations the triamine melted at 176—177°, but further crystallisation led to decomposition.

The triamine, on acetylation, gave rise to a somewhat uncrystallisable product approximating in composition (N = 14·63 per cent.) to an ethenyl anhydro-base,  $NH_2\cdot C_{10}H_5{<}\begin{matrix}N\cdot C_7H_7\\ N:C\cdot CH_3\end{matrix}$. With *p*-nitrobenzenediazonium chloride the base coupled with difficulty, forming a diazoamino-compound.

## *Action of Nitrites on Salts of* 1-p-*Tolyl*-1:2:4-*triaminonaphthalene.*

Alcoholic ethyl nitrite (6 c.c. of a 33 per cent. solution) was added to the triamine (1·6 grams) dissolved in 20 c.c. of alcohol containing 6 c.c. of concentrated hydrochloric acid, when considerable frothing occurred, nitric oxide being evolved; the solution reddened, and a red precipitate slowly separated, whilst the liquid acquired the property of developing an azo-colour with β-naphthol. The red, crystalline precipitate (1·2 grams), which was readily soluble in water, crystallised from the aqueous solution on adding hydrochloric acid in short, dark red needles with a bronzy-green reflex.

The filtrate from these red crystals, when added to alkaline β-naphthol, furnished an azo-compound (1 gram), crystallising from ethyl acetate in garnet-red needles and plates (m. p. 134—135°), which was identified as *p*-tolueneazo-β-naphthol.

The foregoing red hydrochloride was decomposed with cold dilute ammonia when the orange-yellow, crystalline base was recrystallised from benzene or absolute alcohol; it separated from the former solvent in nodules of orange-yellow needles, decomposing at 167°:

0·1423 gave 19·5 c.c. $N_2$ at 13° and 760 mm. N = 16·20.
0·1196 „ 0·3050 $CO_2$ and 0·0536 $H_2O$. C = 69·53; H = 4·98.
$C_{10}H_8ON_2$ requires N = 16·27; C = 69·76; H = 4·65 per cent.

This base is identical in composition with 2-amino-1:4-naphthaquinoneimide obtained by oxidising 2:4-diamino-α-naphthol with ferric chloride. The dark red hydrochloride when crystallised from dilute hydrochloric acid gave Cl = 17·70, the calculated amount for $C_{10}H_8ON_2,HCl$ being Cl = 17·02 per cent.

The foregoing experiment was modified by using ethereal ethyl nitrite, amyl nitrite, and sodium nitrite as sources of nitrous acid, and methyl alcohol and formic acid as solvents. In every case, however, the red hydrochloride was precipitated, even in the presence of copper powder. With sulphuric instead of hydrochloric acid the solution reddened without depositing red crystals, owing to the greater solubility of the sulphate of the amino-quinoneimide. The red precipitate was produced on adding hydrochloric acid.

### *Action of Nitrous Acid on* 2:4-*Diamino-α-naphthol.*

In order to identify the red hydrochloride produced in the foregoing series of experiments a saturated solution of sodium nitrite (0·9 gram) was added to 1 gram of 2:4-diamino-α-naphthol hydrochloride suspended in concentrated hydrochloric acid cooled by a few lumps of ice. On stirring vigorously the salt of the diamine became replaced by red crystals of 2-amino-1:4-naphthaquinoneimide hydrochloride, the yield being practically quantitative.

When treated with alcoholic or ethereal ethyl nitrite or with sodium nitrite, 2-amino-1:4-naphthaquinoneimide hydrochloride was not diazotised even in the presence of excess of mineral acid. Nitrosyl sulphate in 80 per cent. sulphuric acid decomposed the salt, with the formation of a brownish-yellow compound containing only two-thirds as much nitrogen as the original quinoneimide. In no case could any diazotisation of the 2-amino-group be detected.

The sodium nitrite process for preparing 2-amino-1:4-naphthaquinoneimide hydrochloride from 2:4-diamino-α-naphthol hydrochloride compares favourably with the older method of oxidation with ferric chloride (*Annalen*, 1865, **134**, 377; 1870, 154, 312). A specimen prepared with ferric chloride did not depress the melting point of the product obtained by the foregoing method, but was less easily purified from the oxidising agent.

### *Action of Nitrosyl Sulphate on* 1-p-*Tolyl*-1:2:4-*triaminonaphthalene.*

Nitrosyl sulphate (7 grams) was slowly incorporated into an ice-cold solution of the triamine from 3 grams of 2:4-dinitro-1-*p*-

tolyl-α-naphthylamine, dissolved in concentrated sulphuric acid (10 c.c.). Frothing and diazotisation occurred at this stage, and further decomposition of nitrosyl sulphate occurred on adding 4 grams of ice. On adding this solution slowly to 100 c.c. of cold absolute alcohol containing 1 gram of copper bronze, the brown colour changed to yellow, gas was evolved, and a yellow precipitate deposited. After thirty minutes the liquid no longer gave an azo-colour with β-naphthol; the yellow precipitate was then washed with water and crystallised from benzene, when it separated in pale yellow needles decomposing violently at 211—212°:

0·1298 gave 20·8 c.c. $N_2$ at 14° and 746 mm. N = 18·46.
0·1162 „ 0·2952 $CO_2$ and 0·0428 $H_2O$. C = 69·26; H = 4·09.
0·0990 „ 0·2505 $CO_2$ „ 0·0372 $H_2O$. C = 69·06; H = 4·17.
$C_{34}H_{24}O_3N_8$ requires C = 68·92; H = 4·05; N = 18·92 per cent.

This formula corresponds with a substance produced by the combination of two molecular proportions of the *iso*triazole, $C_{17}H_{13}N_3$, with a molecule of nitrogen trioxide, one atom of hydrogen being eliminated from each molecule of triazole. When reduced with zinc and ammonium chloride in dilute alcohol this compound yielded a colourless, oxidisable base, which rapidly became green on exposure to air, and gave yellow salts with the mineral acids, but no diazonium derivative.

The alcoholic filtrate from the foregoing compound and copper powder on dilution with water gave a yellow precipitate readily soluble in benzene, and crystallising therefrom in glistening, orange needles, melting at 234—235°:

0·1172 gave 13·9 c.c. $N_2$ at 749 mm. and 11°. N = 13·91.
$C_{19}H_{17}ON_3$ requires N = 13·86 per cent.

This formula corresponds with an ethoxynaphtha*iso*triazole, $C_2H_5O{\cdot}C_{17}H_{12}N_3$, but the amount of the substance obtained was insufficient for further examination.

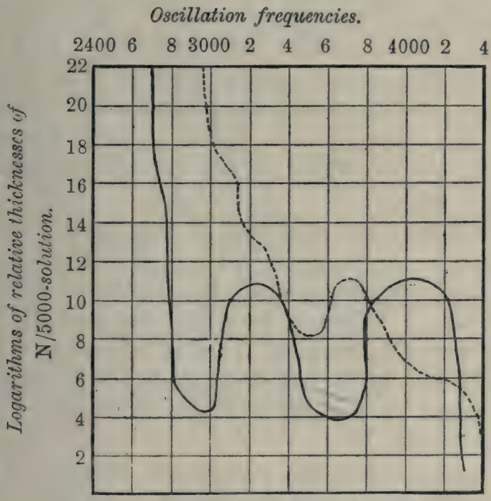
2-p-*Tolyl*-1:2-*naphthatriazole*.—Chromium trioxide (10 grams) dissolved in 20 c.c. of water was added very slowly to a solution of 10 grams of *p*-tolueneazo-β-naphthylamine (m. p. 113°) in 300 c.c. of glacial acetic acid. After two hours the liquid was poured into cold water, and the insoluble, brown product crystallised from glacial acetic acid, when it separated in light yellow, silky needles, melting at 149°:

0·1573 gave 0·4531 $CO_2$ and 0·0730 $H_2O$. C = 78·57; H = 5·16.
0·2403 „ 33·4 c.c. $N_2$ at 15° and 748 mm. N = 16·10.
$C_{17}H_{13}N_3$ requires C = 78·76; H = 5·02; N = 16·22 per cent.

The triazole agrees in properties with the compound obtained by

Charrier on heating *p*-tolueneazo-β-naphthylamine to 300° (*Atti R. Accad. Sci. Torino*, 1910, **45**, 131).

3-*p*-Tolyl-1 : 2-naphtha*iso*triazole (Ullmann, *loc. cit.*) was prepared by adding sodium nitrite to a solution of 2-*p*-tolyl-1 : 2-naphthylenediamine in glacial acetic acid or in alcohol containing hydrochloric acid. When crystallised from alcohol or light petroleum it decomposed at 146—147°. Repeated crystallisation of this substance led to a loss of nitrogen, and the melting point gradually rose to that of 1 : 2-naphthamethylcarbazole (m. p. 181°). Analysis of the *iso*triazole decomposing at 146—147° gave C=78·91, H=5·15, N=16·37, theory for $C_{17}H_{13}N_3$ requiring C=78·76, H=5·05, N=16·22 per cent. The melting point previously recorded for this substance (P., 1910, **26**, 151) was that of a specimen which, as a result of repeated crystallisation, had undergone partial decomposition.



——— 2-p-*Tolyl-αβ-naphthatriazole.*
- - - - - - 3-p-*Tolyl-αβ-naphtha*iso*triazole.*
(2-p-*Tolyl*-1 : 2-*naphthylenediazoimine*).

*Absorption Spectra.*—The two foregoing isomerides were examined spectroscopically in absolute alcohol. The triazole showed two strong bands, with the heads at 1/λ 2950 and 1/λ 3650. The *iso*triazole gives one shallow band at 1/λ 3500.

We desire to express our thanks to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation

Royal College of Science for Ireland.
Dublin.

# XII.—*Co-ordination Compounds of Vanadium. Part I. The Acylacetonates.*

By Gilbert T. Morgan and Henry Webster Moss,
A.I.C., A.R.C.Sc.I.

The resolution of certain co-ordination compounds of cobalt, chromium, iron, and rhodium into optically active components by Werner and his collaborators has placed on a firm experimental basis the conception of octahedral symmetry as exhibited by these substances, and has facilitated the extension of stereochemical considerations to the chemical constitution of inorganic compounds in general. Two types of co-ordination compounds have been mainly studied from the stereochemical point of view, namely, those in which four and six molecules or radicles are segregated round a central metallic atom.

In the former case the existence of two isomerides having the formula $PtCl_2,2NH_3$ is taken to indicate that the arrangement of the co-ordination complex around the platinum atom is in one plane, this grouping differing from the tetrahedral arrangement characterising carbon compounds. It is of interest to note, however, that even in the case of carbon compounds the plane configuration has been indicated as a passing phase to explain racemisation (Garner, P., 1912, **28**, 67).

In the case of co-ordination compounds containing six radicles or molecules segregated round the central metallic atom as in the case of the hexammine and pentammine (luteo- and purpureo-) chlorides of cobalt and chromium and many other complex salts of these metals, it can scarcely be doubted in the light of present experimental knowledge that the spacial arrangement of these segregating radicles or molecules is that of the octahedron.

*Influence of Atomic Volume on Co-ordination.*—With the great majority of complex inorganic salts the co-ordination number is either four or six, although in certain instances, for example, potassium molybdenum cyanide, $K_4[Mo(CN)_8]$, the co-ordination complex contains eight cyanide groups.

In a recent communication (*Ber.*, 1912, **45**, 1322) Ephraim has considered the influence of atomic volume on the stability of metallic ammine-chlorides having the general formula $R^{II}Cl_2,6NH_3$, and shows that the dissociation pressure of these substances at any fixed temperature, or the dissociation temperature at any fixed pressure, is closely related to the atomic volume of the metal. Those metals with the smallest atomic volume give the most stable hexaammines, and, in fact, no metallic elements with atomic volumes greater than 14 yield compounds of this type which are stable at the ordinary temperature.

On the other hand, metals with high atomic volumes, such as the metals of the alkaline earths (A.V. of Ca=25, Sr=35, Ba=36·5), yield ammine-chlorides of the type $RCl_2,8NH_3$, whilst zirconium and thorium (A.V. of Zr=21·7, Th=21) give rise to the chlorides $RCl_4,8NH_3$, from which it would appear that a large atomic volume, whilst decreasing the stability of the complex ammine-salt, leads to an increase in the co-ordination number, irrespective of the value of the principal valency of the metal, since both bivalent and quadrivalent elements give co-ordination compounds of the same order of complexity.

The recognition of co-ordination in inorganic compounds renders necessary a revision of our views on valency. Werner assumes that in addition to principal valencies, which can usually be ascertained by electrolytic means, the central metallic atom possesses a set of auxiliary valencies ("Nebenvalenzen") which function in the formation of co-ordination compounds. These auxiliary valencies, like the principal valencies, are apparently to be regarded as integral, so that in its hexammine salts $(Co,6NH_3)Cl_3$, cobalt has a principal valency of 3 and an auxiliary valency of 6, whereas in the pentammine salts, $(Co,5NH_3{\cdot}Cl)Cl_2$, the metal exerts an auxiliary valency of 5 whilst retaining its principal valency of 3, one of these principal valencies being now implicated in the co-ordination complex.

These hypotheses involve the assumption that chemical affinity is always manifested by valencies which are exact multiples of the adopted unit of valency, namely, that of a univalent atom or group. It seems, however, highly probable that the valencies of elements are not exactly whole numbers, and that even when the integral portions of the valencies have been satisfied there may still remain fractional parts which may, under certain conditions, become operative in the formation of complex substances. This residual affinity may be sufficiently powerful to induce the aggregation which occurs in co-ordination compounds.

If chemical affinity is regarded as an attractive force proceeding equally in all directions from the centre of the sphere occupied by an atom, then the smaller the volume the greater will be the concentration of chemical affinity over its surface and the greater will be the effectiveness of the atom in inducing co-ordination.

Moreover, if chemical affinity is a force which falls off rapidly with the distance from the centre of the atomic sphere, and it may quite conceivably vary inversely as the square, or even as some higher power of the distance, then a comparatively slight alteration in atomic volume will produce a very marked effect on the stability of the co-ordination compound.

The forces to which these compounds owe their existence cannot be regarded as emanating entirely from the central atom; the residual affinity of this element simply serves as a determining factor. The stability of the arrangement thus initiated is dependent on the mutual attractions exerted on one another by the co-ordinating radicles or groups. It is precisely those radicles or groups which possess considerable residual affinity which function most frequently in the formation of co-ordinated complexes. The general tendency to form hydrated and ammoniated metallic salts is to be attributed in the main to the capacity for association exhibited by water and ammonia molecules respectively. The presence of carbonyl, cyanide, nitrite, and sulphite groups in many stable complexes is similarly to be correlated with the unsaturated nature of these radicles, as contrasted with the saturated carbonate, nitrate, and sulphate groups, which figure less prominently in co-ordination compounds and give rise to less stable aggregations. The halogen radicles appear in many co-ordinated complexes by virtue of their higher valencies.

The size of the atomic volume of the central element has a threefold influence on the stability of the co-ordination compounds. First, if the atomic volume is small the residual affinity of the atom is exerted in a more concentrated form. Secondly, the co-ordinating molecules or radicles can approach nearer to the centre of the central atom when its volume is small and therefore nearer to one another, so that their mutual attractions become more effective. Thirdly, as the dimensions of the co-ordinating molecules or radicles are of molecular or atomic magnitude, these segregating units will fill more completely the available space round an atom of small volume than that round an atom occupying a larger sphere. This filling up of the available space also conduces to stability, as is manifested by many stereoisomeric compounds.

These speculations are justified by the known facts in regard to co-ordination compounds. The metals forming the most stable complexes are those of the eighth periodic family and their neighbours, and it is precisely these elements among the metals which have the lowest atomic volumes. The three triplets of this group of metals appear each at points of minima on the atomic-volume curve. On the other hand, the alkali metals appearing at points of maxima on this curve give rise to very few co-ordination compounds which are generally extremely unstable.

### *Symmetrical Arrangement of Co-ordination Units about the Central Atom.*

If the determining factor in co-ordination is the residual affinity of the central atom which has not necessarily an integral value, and if the formation of the complex is due in part to the mutual attractions of the associating units, then the question arises, what will be the most likely number of units to segregate round the central atom? It is obvious that the most stable system will be that in which there is a symmetrical distribution of the forces interacting between the associating units, and this condition is attained by taking such a number of units that they can be arranged symmetrically over the surface of a sphere. This problem has but few solutions, inasmuch as there are only five regular solids, the tetrahedron, octahedron, cube, icosahedron, and pentagonal dodecahedron, with 4, 6, 8, 12, and 20 vertices respectively. These integers will be the co-ordination numbers corresponding with the theoretically possible most stable systems, and there is ample justification for the belief that molecular aggregations exist corresponding with four of these cases of symmetry, that is, with all the possible cases, except perhaps that of the dodecahedron.

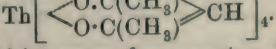
*Tetrahedral Symmetry.*—The tetrahedron is the form governing the arrangement of units round the carbon atom, and it is noteworthy that this non-metal has the least atomic volume of all the elements. With a larger atomic volume and a segregation of four units there is apparently a tendency for this symmetrical configuration to be replaced by a less regular plane arrangement as in the platino- and pallado-ammines. This plane arrangement has already been referred to as a passing phase for carbon compounds (Garner, *loc. cit.*).

*Octahedral Symmetry.*—The octahedron is the form corresponding with the vast majority of metallic co-ordination compounds, including most of the very stable complexes of the metals of the eighth periodic family. The isolation of enantiomorphous modifications of such substances as $[\mathrm{Co,2C_2H_4(NH_2)_2,Cl_2}]\mathrm{Cl}$ and

$$[\mathrm{Co,2C_2H_4(NH_2)_2,2NH_3}]\mathrm{Cl_3},$$

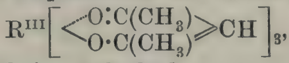
is a brilliant confirmation of the existence of this type of symmetry (Werner, *Ber.*, 1911, **44**, 3281; 1912, **45**, 3287).

*Cubic Symmetry.*—The cube would correspond with the arrangement of groups in such compounds as the following: $\mathrm{K_4Mo(CN)_8}$, $\mathrm{R^{II}Cl_2,8NH_3}$, $\mathrm{RCl_4^{IV},8NH_3}$, $\mathrm{NMe_3Et[I\,I_8]}$, $\mathrm{K_4Th(C_2O_4)_4}$, and



$$\mathrm{Th}\left[<\begin{matrix}\mathrm{O{:}C(CH_3)}\\ \mathrm{O{\cdot}C(CH_3)}\end{matrix}>\mathrm{CH}\right]_4.$$

Substances having this type of symmetry have been much less extensively studied than those of the octahedral group, and their investigation will probably show that they present characteristic types of isomerism. Thorium quadriacetylacetonate, for example, should exist in two stereoisomeric non-enantiomorphous modifications, differing in this respect from the teracetylacetonates,



$$R^{III}\left[<\begin{matrix}O{:}C(CH_3)\\ O{\cdot}C(CH_3)\end{matrix}>CH\right]_3,$$

which on account of their octahedral symmetry should be resolvable into optically active enantiomorphous components.

*Icosahedral Symmetry.*—The icosahedron corresponds with the segregation of twelve associating units round a central atom of which the following complex salts may be examples: the alums, $[R''',12H_2O]SO_4{\cdot}SO_4R'$; the double chlorides, $[Mg,12H_2O]PtCl_6$; $[Mn,12H_2O](AuCl_4)_2$; and the phosphomolybdates,

$$(NH_4)_3[PO_4,12MoO_3].$$

*Less Symmetrical Aggregations.*—The question now arises whether these symmetrical groupings are the only arrangements which obtain throughout the whole range of compounds exhibiting co-ordination.

It might conceivably happen that the atomic volume of an element would be such that the circumjacent space could accommodate a number of associating units not corresponding with any one of the co-ordination numbers derived from the foregoing four regular solids. The arrangement, although not completely symmetrical, might in certain circumstances be capable of existence. Thorium, with an atomic volume of 21, forms the double carbonates $[Th(CO_3)_5](NH_4)_6$ and $[Th(CO_3)_5]Tl^{I}_6$. The carbonate group generally functions as two associating units, and accordingly these salts may correspond with the arrangement of ten points on a sphere, and with this number of associating units a certain degree of symmetry can be attained.*

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* Dr. J. P. Johnston has kindly prepared a model illustrating one of two ways in which a polar symmetry can be developed with this number of points. Two points are taken at the ends of a diameter of a sphere, and round each of these points a small circle is described at an angular distance of 59°15′. Squares are inscribed in these circles so that the directions of the diagonals of one are parallel to the bisectors of the angles between the diagonals of the other. The angular distances between consecutive vertices of one square are then equal to the angular distances of its vertices from the adjacent vertices of the other. These angular distances are 74°51′ approximately. The solid formed by joining the ten points has sixteen triangular faces, each face being an isosceles triangle.

A second arrangement is obtained by describing the circles so that each vertex of the inscribed square is at an angular distance of 65°30′ from the adjacent polar point and from each of the adjacent vertices of the other square. The relative orientation of the two squares is the same as in the previous arrangement. The angular distance between consecutive vertices of the same square will then be 79°32′ approximately.

Among the elements of the fifth periodic family there are instances of complexes in which it is not easy to bring the co-ordination number into line with the symmetrical groupings based on the octahedron or cube.

In the double fluorides and oxyfluorides it is generally assumed that fluorine and oxygen each function as a single associating unit, as, for example, in Marignac's well known isomorphous series: $K_2TiF_6,H_2O$, $K_2CbOF_5,H_2O$, and $K_2WO_2F_4,H_2O$. It seems reasonable to suppose that these compounds all possess the octahedral symmetry, the co-ordinated complexes being composed in each case of six associating units, $F_6$, $OF_5$, and $O_2F_4$, with oxygen as the spacial equivalent of fluorine in the oxyfluorides.

Although in the foregoing example columbium falls into line with titanium and tungsten in giving the six-membered complex, yet the assumption that oxygen is the spacial equivalent of fluorine does not lead in general to octahedral symmetry in the case of the allied metal, vanadium.

The vanadyl double oxalates and thiocyanates,

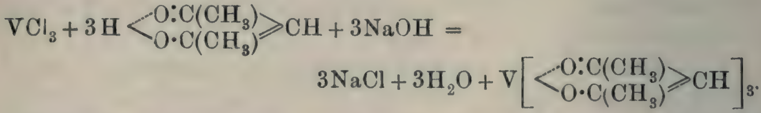
$$[VO(C_2O_4)_2]R_2^I,2H_2O \text{ and } [VO(CNS)_4]R_2^I,5H_2O,$$

contain five associating units in their complexes, and a similar arrangement obtains in the following isomorphous double fluorides and oxyfluorides: $VF_3,R^{II}F_2,7H_2O$, $VOF_2,R^{II}F_2,7H_2O$, and

$$VO_2F,RF_2,7H_2O.$$

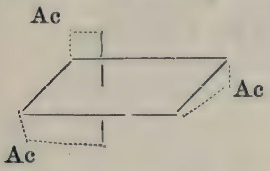
Here the co-ordination groups would appear to be 5F, $OF_4$, and $O_2F_3$ respectively. Werner has recognised this difficulty, and endeavours to meet it by bringing a molecular proportion of water into the co-ordination complex, formulating the oxyfluorides $VOF_2,RF_2,7H_2O$ as $[R,6H_2O][VOF_4,H_2O]$, in which there are six associating units round the vanadium atom. This formulation could be applied to all the foregoing double salts, since they all contain water of crystallisation, but it is not available in the case of the vanadyl acylacetonates described in the present communication, as these compounds crystallise without water from many anhydrous organic solvents.

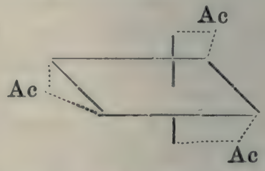
Anhydrous vanadium trichloride (1 mol.) and acetylacetone (3 mols.) interact in absolute alcohol in the presence of sodium hydroxide or ethoxide (3 mols.), giving rise to vanadium teracetylacetonate. As it has not been found possible to combine vanadium directly with carbon through the agency of the Grignard reaction, it is, in the highest degree, probable that in this condensation acetylacetone reacts in its enolic form, so that the metallic atom becomes attached to enolic oxygens by three of its principal valencies, each unsaturated acetylacetonate group functioning as two associating units, so that a six-membered complex is developed having octahedral symmetry:



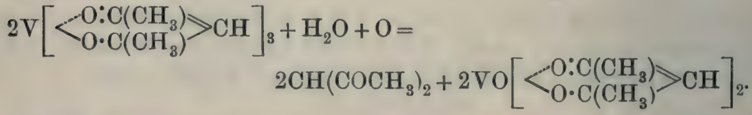
$$\mathrm{VCl_3 + 3H}{<}\begin{matrix}\mathrm{O{:}C(CH_3)}\\ \mathrm{O\cdot C(CH_3)}\end{matrix}{>}\mathrm{CH + 3NaOH} = \mathrm{3NaCl + 3H_2O + V}\left[{<}\begin{matrix}\mathrm{O{:}C(CH_3)}\\ \mathrm{O\cdot C(CH_3)}\end{matrix}{>}\mathrm{CH}\right]_3.$$

Similar condensations occur with benzoylacetone and acetylmethylacetone, and the products are in all probability racemic compounds containing two enantiomorphous components:





By oxidation with moist air the vanadium teracylacetonates give rise to the vanadyl bisacylacetonates, substances which can also be produced by the direct condensation of vanadyl dichloride and the corresponding acylacetone:



$$\mathrm{2V}\left[{<}\begin{matrix}\mathrm{O{:}C(CH_3)}\\ \mathrm{O\cdot C(CH_3)}\end{matrix}{>}\mathrm{CH}\right]_3 + \mathrm{H_2O + O} = \mathrm{2CH(COCH_3)_2 + 2VO}\left[{<}\begin{matrix}\mathrm{O{:}C(CH_3)}\\ \mathrm{O\cdot C(CH_3)}\end{matrix}{>}\mathrm{CH}\right]_2.$$

These vanadyl bisacylacetonates are soluble in the ordinary organic media, except ether. Their molecular complexity corresponds with the simplest empirical formula, since a molecular-weight determination in chloroform showed that vanadyl bisacetylacetonate is not associated. The ultraviolet absorption spectra of these compounds agree very closely with those of the teracylacetonates, and also with those of the acylacetones, a relationship which seems to indicate that the acylacetonate group is in a similar condition in all these substances.

The question now arises, What is the arrangement of the five associating units about the central vanadium atom? Do they form a five-membered complex, or does the group VO function as a single co-ordinating centre attracting to itself four associating units which may be arranged in one plane, as in the case of the platino-ammines? In either alternative there appears to be a departure from the normal symmetrical arrangement based on the octahedron.

The atomic volume of vanadium (9·3) is considerably greater than that of chromium (7·7), and its co-ordination compounds confirm the foregoing assumption as to the relationship between atomic volume and co-ordination in being less stable than the complexes containing chromium. In aqueous solution the double thiocyanates,

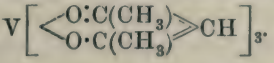
$R_3V(CNS)_6$, are almost entirely dissociated (Cioci, *Zeitsch. anorg. Chem.*, 1899, **19**, 308). Vanadium in the form of the trichloride combines, however, with pyridine and other organic bases, and the products are being examined with the object of obtaining further evidence as to the co-ordination values which obtain in the case of this element.

## Experimental.

The anhydrous vanadium chloride employed in the following operations was prepared by heating vanadic anhydride in a stream of carbon disulphide vapour until the residue consisted entirely of vanadium trisulphide. This substance was then heated in a current of chlorine, when sulphur chloride and vanadium tetrachloride distilled over, and were separated by fractionation. During these distillations a portion of the tetrachloride dissociated into vanadium trichloride and chlorine, the unchanged tetrachloride was heated in a reflux apparatus until the brown liquid disappeared, and a dry residue of vanadium trichloride was obtained as a dark purple mass entirely soluble in absolute alcohol, although insoluble in dry Grignard ether (Kay, T., 1880, **37**, 728; Halberstadt, *Ber.*, 1882, **15**, 1619). It has been stated that anhydrous vanadium trichloride is soluble in ether to a green solution. We find, however, that in the absence of water or alcohol the dry chloride is insoluble in this medium.

The more volatile fractions obtained in the foregoing distillations contained in addition to sulphur chloride small quantities of a very volatile vanadium derivative, which was not further examined.

### *Vanadium Teracetylacetonate,*



$$V\left[<\begin{matrix}O{:}C(CH_3)\\O{\cdot}C(CH_3)\end{matrix}>CH\right]_3.$$

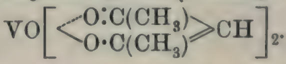
This compound was prepared most conveniently by adding aqueous sodium carbonate (1·5 mols.) to a mixture of acetylacetone (3 mols.), vanadium trichloride (1 mol.), and chloroform. The co-ordination product, which dissolved in the organic solvent, was isolated by rapid concentration of the solution to a small bulk at the ordinary temperature. The transparent, dark brown prisms or square plates thus obtained were washed with cold alcohol, in which they are somewhat soluble, and were dried on the water-bath in an atmosphere of carbon dioxide:

0·1500 gave 0·2832 $CO_2$ and 0·0926 $H_2O$. C=51·5; H=6·86.
0·1000 ,, 0·0262 $V_2O_5$. V=14·67.
$C_{15}H_{21}O_6V$ requires C=51·7; H=6·0; V=14·7 per cent.

The teracetylacetonate was also prepared by adding the calculated amount of alcoholic sodium hydroxide (3 mols.) to a solution of vanadium trichloride (1 mol.) and acetylacetone (3 mols.) in absolute alcohol. The filtrate from sodium chloride was concentrated in carbon dioxide, and the transparent, dark brown prisms which separated were recrystallised from dry ether. The substance is insoluble in water, and dissolves freely in chloroform or benzene; it crystallises from warm acetylacetone in large, well-defined, dark brown plates and prisms. Vanadium teracetylacetonate melts indefinitely at 185—190°,* and can be distilled in small quantities without decomposition.

In the moist condition the teracetylacetonate readily takes up oxygen, and loses a molecular proportion of acetylacetone. During this oxidation the square plates or prisms retain their shape, so that green pseudomorphs after the original compound are produced, consisting of the following vanadyl derivative.

### *Vanadium Oxybisacetylacetonate* (*Vanadyl Bisacetylacetonate*),



$$\mathrm{VO}\left[<\begin{matrix}\mathrm{O{:}C(CH_3)}\\ \mathrm{O\cdot C(CH_3)}\end{matrix}>\mathrm{CH}\right]_2.$$

The aerial oxidation of vanadium teracetylacetonate leads to the production of vanadium oxybisacetylacetonate, and this substance can also be prepared by the following method, which is applicable to vanadyl derivatives of other β-diketones.

Vanadic anhydride is reduced to vanadyl chloride by boiling with concentrated hydrochloric acid and alcohol. The blue solution thus obtained is exactly neutralised with aqueous sodium carbonate, the precipitated grey vanadyl hydroxide is washed successively with water and alcohol, and while still moist is dissolved in a warm alcoholic solution of acetylacetone. The green solution on cooling deposits small, bluish-green crystals of vanadium oxybisacetylacetonate, which are washed with alcohol until free from the brown mother liquor. The compound separates from benzene, chloroform, or hot alcohol in hard, transparent, flattened, bluish-green prisms, which are insoluble in water, sparingly soluble in alcohol, and dissolving very readily in chloroform. Although practically insoluble in dry ether, this and the following vanadyl compounds undergo a slight decomposition on digestion with this solvent, a small amount of resinous matter passing into solution:

0·1500 gave 0·2476 $CO_2$ and 0·0790 $H_2O$. C=45·02; H=5·86.
0·1500 „ 0·2488 $CO_2$ „ 0·0758 $H_2O$. C=45·24; H=5·66.

---

* The melting point (265—266°) given in the preliminary note (P., 1912, **28**, 199) was rendered too high by the presence of the oxidation product, vanadyl bisacetylacetonate.

0·1130 gave 0·0380 $V_2O_5$. V=18·65.

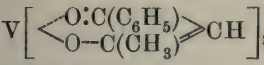
$C_{10}H_{14}O_5V$ requires C=45·3; H=5·3; V=19·2 per cent.

Molecular-weight determinations in chloroform by the ebullioscopic method showed that the compound has the simple formula:

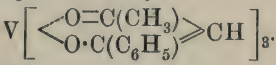
0·1962 in 17·41 $CHCl_3$ gave $\Delta t=0·161°$. M.W.=256.
0·1688 „ 17·41 $CHCl_3$ „ $\Delta t=0·139°$. M.W.=255.
$VO(C_5H_7O_2)_2$ requires M.W.=265.

The bisacetylacetonate has no definite melting point, but decomposes and chars at high temperatures.

### *Vanadium Terbenzoylacetonate,*


$\mathrm{V}\left[\left\langle\begin{matrix}\mathrm{O{:}C(C_6H_5)}\\ \mathrm{O{-}C(CH_3)}\end{matrix}\right\rangle\mathrm{CH}\right]_3$

or

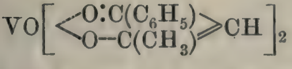

$\mathrm{V}\left[\left\langle\begin{matrix}\mathrm{O{=}C(CH_3)}\\ \mathrm{O{\cdot}C(C_6H_5)}\end{matrix}\right\rangle\mathrm{CH}\right]_3$.

When alcoholic solutions of vanadium trichloride (1 mol.) and benzoylacetone (3 mols.) are mixed, the green colour of the former substance disappears, and the liquid acquires a clear, brown tint. The addition of alcoholic sodium ethoxide (3 mols.) determines the precipitation of the brown co-ordination compound mixed with sodium chloride. The organic substance was extracted from this precipitate with chloroform, the filtered solution evaporated to dryness, and the resinous residue dissolved in benzene, from which the terbenzoylacetonate separated in dark, chocolate-brown leaflets, melting at 218—220°:

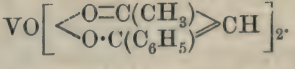
0·1500 gave 0·3632 $CO_2$ and 0·0784 $H_2O$. C=66·36; H=5·80.
0·2000 „ 0·0338 $V_2O_5$. V=9·46.
$C_{30}H_{27}O_6V$ requires C=67·4; H=5·1; V=9·58 per cent.

The terbenzoylacetonate is insoluble in water, sparingly soluble in alcohol or ether, and dissolves very freely in benzene or chloroform. It is somewhat less oxidisable than the teracetylacetonate, but is slowly decomposed on exposure to moist air, so that after three months a specimen had become largely converted into the bright green vanadium oxybisbenzoylacetonate mixed with long, colourless needles of benzoylacetone.

### *Vanadium Oxybisbenzoylacetonate (Vanadyl Bisbenzoylacetonate),*


$\mathrm{VO}\left[\left\langle\begin{matrix}\mathrm{O{:}C(C_6H_5)}\\ \mathrm{O{-}C(CH_3)}\end{matrix}\right\rangle\mathrm{CH}\right]_2$

or

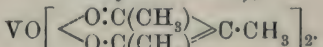

$\mathrm{VO}\left[\left\langle\begin{matrix}\mathrm{O{=}C(CH_3)}\\ \mathrm{O{\cdot}C(C_6H_5)}\end{matrix}\right\rangle\mathrm{CH}\right]_2$.

Although formed by the aerial oxidation of the preceding compound, this substance is best obtained by the direct interaction of vanadyl hydroxide and benzoylacetone. When the freshly precipitated hydroxide, after washing with water and alcohol, is warmed with an alcoholic solution of benzoylacetone in slight excess, the hydroxide dissolves, and the resulting green solution deposits immediately emerald-green leaflets of vanadium oxybisbenzoylacetonate:

0·1500 gave 0·3362 $CO_2$ and 0·0788 $H_2O$. C=61·12; H=5·82.
0·1500 „ 0·3296 $CO_2$ „ 0·0627 $H_2O$. C=59·92; H=4·65.
0·2446 „ 0·0590 $V_2O_5$. V=13·5.
0·1334 „ 0·0324 $V_2O_5$. V=13·7.
$C_{20}H_{18}O_5V$ requires C=61·69; H=4·62; V=13·11 per cent.

The compound is insoluble in water or ether, sparingly soluble in alcohol, more so in benzene, and very soluble in chloroform. It crystallises from a mixture of chloroform and alcohol in bright green leaflets melting at 214—215°.

### *Vanadium Oxybisacetylmethylacetonate (Vanadyl Bisacetylmethylacetonate)*,



$$VO\left[<\begin{matrix}O{:}C(CH_3)\\O\cdot C(CH_3)\end{matrix}>C\cdot CH_3\right]_2.$$

This substance was prepared by the method employed for the other two vanadyl derivatives, freshly precipitated vanadyl hydroxide being dissolved in an alcoholic solution of acetylmethylacetone. It is very soluble in chloroform, sparingly so in alcohol, and insoluble in water or ether. From benzene it crystallises in sage-green, acicular prisms, which decompose and char on heating:

0·1490 gave 0·2740 $CO_2$ and 0·0860 $H_2O$. C=50·33; H=6·5
0·1733 „ 0·0535 $V_2O_5$. V=17·2.
$C_{12}H_{18}O_3V$ requires C=49·3; H=6·2; V=17·4 per cent.

Vanadium teracetylmethylacetonate was produced in alcoholic solution by the interaction of vanadium trichloride, acetylmethylacetone, and sodium ethoxide; it is a brown, easily decomposable substance, readily taking up oxygen and passing into the preceding vanadyl compound.

### *Comparative Study of the Absorption Spectra of Vanadium Trichloride, the β-Diketones, and their Co-ordination Products.*

The compounds were dissolved in absolute alcohol to *N*/1000-solutions, and examined in thicknesses of 2, 4, 5, 10, 15, 30, 40, and 50 mm.; the dilution was continued to *N*/5000-solutions, and photographs were taken again at the foregoing thicknesses. The instrument was a one-prism Hilger spectrometer, and the iron arc was used as the source of light.

The ultraviolet absorption spectra of the foregoing acylacetonates were photographed, and compared with those of their generators, vanadium trichloride, vanadyl dichloride, acetylacetone, acetylmethylacetone, and benzoylacetone. Absorption curves were plotted, and those for the acylacetones themselves were found to agree with the results obtained for these substances by Baly and Desch (T., 1904, **85**, 1029; 1905, **87**, 766).

FIG. 1.

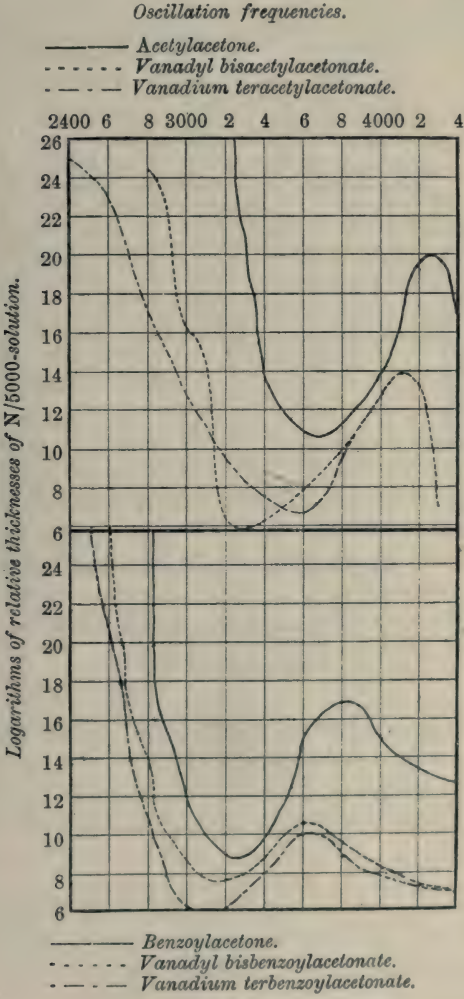
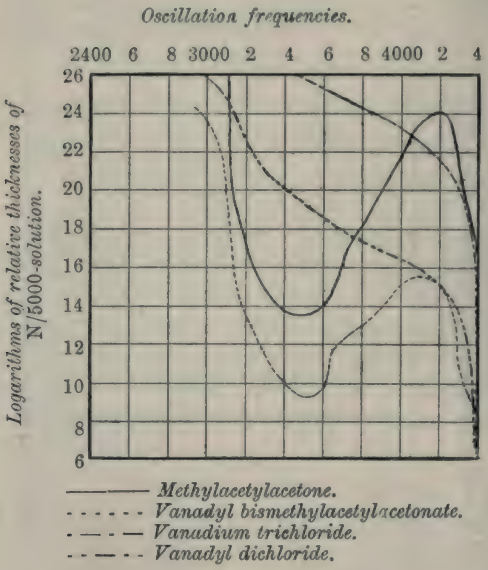


FIG. 2.

The curves for vanadium teracetylacetonate and vanadyl bisacetylacetonate are closely related, and correspond in general form with the curve for acetylacetone, except that they are shifted towards the red end and the absorption bands are persistent at greater dilutions (Fig. 1). The curves for vanadium terbenzoylacetonate and vanadyl bisbenzoylacetonate are almost superposable, that of the former compound being slightly more towards the red, with a somewhat more persistent band (Fig. 2). A similar relationship holds between the bands of acetylmethylacetone and vanadyl bisacetylmethylacetonate (Fig. 3).

On the other hand, it will be noticed that at these dilutions the inorganic generators of these co-ordination compounds, vanadium trichloride and vanadyl dichloride, show no absorption bands, but merely general absorption, the curve of the former compound being much further into the ultraviolet than that of the vanadyl compound.

FIG. 3.



The authors desire to express their thanks to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

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DUBLIN.

# XIII.—*Chemical Reactivity and Absorption. Part II. The Variation of Absorption with Concentration.*

By Edward Charles Cyril Baly and Francis Owen Rice.

In two recent papers (Baly and Krulla, T., 1912, **101**, 1469; Baly and Rice, *ibid.*, p. 1475) an explanation of the phenomena of ultraviolet absorption was put forward. It was pointed out that if the affinities of the various atoms in any molecule be considered, it will be evident that a single free molecule must be the centre of a field of force due to the condensation together of the force-lines having their origin in the affinities of the atoms. Clearly the chemical reactivity of any molecule must depend on the free existence of the atomic affinities, and therefore the formation of these condensed force-fields will cause a great decrease in the affinity and the reactivity. If the balance of affinities of opposite type, basic and acidic, within any molecule be complete, then the condensation of the force-lines due to them will also tend to be complete. Such molecules will possess a vanishingly small reactivity.

This condition occurs in the case of simple molecules such as HCl and $NH_3$, $CO_2$ and CaO, and in this is to be found the explanation of the fact that such pairs of substances do not react together in the pure dry state. If the condensed systems be unlocked by some means, then the affinities will become free, and chemical reactivity will begin to make its appearance. One of the possible means of opening up these condensed systems is by the admixture of other molecules possessing residual affinity, that is to say, molecules in which the opposite types of affinity are not balanced, so that after the maximum condensation possible has taken place there is left over a residue. The lines of force due to this residual affinity will interpenetrate the closed systems of the unreactive molecules, with the result that they will become opened partly or wholly, and they will develop chemical reactivity towards other similarly-opened systems. For this reason the extraordinary influence of water-vapour in causing the above pairs of substances to unite together may be understood.

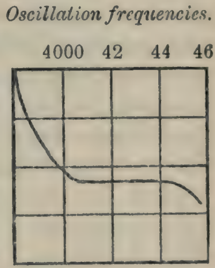
Again, it appears that light waves also are able in many cases to open the closed systems, for we have definite evidence that many chemical reactions, such as, for example, the union of hydrogen and chlorine, are catalysed by the light rays. Inasmuch as the light in opening the system is doing work against chemical forces, this gives us a rational explanation of the selective absorption of light.

A point of some considerable interest may be noted in connexion with the closed field of force surrounding a complex molecule. It is evident that in such a case as this the potential gradient within the closed field will be complex, and the tendency will be for the solvent or the light waves to attack that portion of the system where the potential gradient is the steepest. This at once suggests the fact that a complicated system such as must surround the more complex molecules will be opened in stages, and on this conception was based a theory of fluorescence, and some definite evidence was brought forward in strong support of it.

Although, as has been pointed out, light waves have the power of opening the systems, it does not necessarily follow that light alone should always be able to open a system, especially if the substance in question is in the absolutely pure state. On the other hand, such substances as are very little affected by light rays in the pure state may have their systems sufficiently opened by means of a solvent for the light rays to act on them and to open their systems still further. This point is capable of direct observation, because it is perfectly possible to measure quantitatively the amount of light absorbed by a given quantity of a substance, both in the pure state and also in solution in some diactinic solvent. It is evident that if the closed system of a substance were opened up by means of solution in some solvent, the quantity of light absorbed by the substance in the pure state and in solution would be different. In fact, this would afford a reasonable explanation of the progressive variation that has so frequently been observed from Beer's law. It would follow from the conception here put forward that in the case of a substance, the closed field of force of which is opened by a solvent, the amount of light absorbed should increase with the dilution, provided, of course, that the thickness of the solution were comparable. In the ideal case one would expect the following series of phenomena to be realised. If the quantity of light absorbed by a given thickness of the pure substance were measured, then, according to Beer's law, this quantity should also be absorbed by double the thickness of a solution in some diactinic solvent of that substance with a concentration of 50 per cent., and so on. On the other hand, if the solvent tends to open the closed force fields of the substance in question, then the absorption of the solution will be greater than that of the pure substance. Further, the absorption should increase with further dilution until a maximum is reached. If the dilution be still further increased, the absorption should then diminish until it finally vanishes. It must clearly be understood that this series of phenomena can only be observed if a single simple condition of opening up the closed field of force comes into play. If on increasing the dilution a second stage of the opening up is involved, it is manifest that the above quantitative relations will not hold.

We have made several quantitative investigations of the amount of light absorbed, and we find that the facts observed are very similar to those which the theory led us to expect.

Strictly speaking, such observations as these should be made by means of a spectrophotometer, but as our observations dealt with ultraviolet absorption it was not found possible to devise a satisfactory spectrophotometer for this purpose. The substance most completely investigated by us was ethyl acetoacetate, the absorption curve of which is shown in the figure, and although we were not able to make direct spectrophotometric measurements, yet it is evident that the height on the ordinate at which the step-out on the absorption curve appears will give a relative measure of the amount of light absorbed. In other words, by comparing together these heights obtained under different conditions of solution we were able to observe these thicknesses of material which just allowed the light to pass through, and these thicknesses at once give a quantitative relation of the amount of light absorbed. It will be understood that this will depend entirely on the constancy of the source of light used, for if any variation takes place in the intensity of the source of light used it is evident that inaccurate values will at once be obtained. The source of light used in our experiments was the electric spark between carbon poles which had been boiled successively in concentrated solutions of uranium nitrate and ammonium molybdate and heated to redness after each such treatment.



In using this source it was found that exceedingly constant results were obtained. A further point of difficulty was at first met with in the developing of the photographic plates after exposure, but this was readily overcome by always using the same strength of developer and leaving the plates in this solution for the same time in every case. We then had little difficulty in obtaining perfectly constant results. In order to ensure the greatest accuracy, as many comparative exposures as possible were taken on the same plate, so that every one of these was subject to the same conditions in development.

In the measurements of the absorption of the pure substances and their concentrated solutions it was, of course, necessary to use very thin layers, and for this purpose a special cell was designed and made for us by Hilger, somewhat resembling that used by Purvis in his work on the absorption of pure substances. The cell consists of two quartz plates, which are similar to those used in the Perot and Fabry interferometer. Each plate is about 10 mm. thick, and whilst one is mounted on a rigidly fixed stand, the other is mounted on a very accurate micrometer screw, so that the distance between the two can be adjusted. The micrometer screw is provided with a vernier by means of which the distance between the plates can be read to 0·001 mm., and the whole mounting is very massive, so that there is little danger of displacement when very thin films of liquid are employed owing to the pressure due to surface tensions.

Before any experiments were done the zero of the instrument was checked by bringing the two quartz plates as close together as possible, and observing the set of interference fringes produced by the air layer between them.

It has already been said that the relative amounts of light absorbed by the substance under investigation were obtained by a comparison of the thickness through which the light rays corresponding with the absorption band were just transmitted, for example, in the case of ethyl acetoacetate a $N/2000$-solution in alcohol, this transmission just took place at a thickness of 30 mm., that is, in plotting the absorption curve of a $N/2000$-solution the head of the absorption band was found at 30 mm.; at $N/1000$-concentrations this step-out was found with a thickness of 15 mm. With $N/200$- or $N/20$-solutions the thicknesses at which the step-out occurred were 0·3 mm. and 3 mm. respectively.

It will be seen that these thicknesses are inversely proportional to the concentration, and therefore over this range of concntration Beer's law holds good. On the other hand, in the case of a $N/2$-solution the thickness at which the step-out occurred was found to be 0·05 mm., when, of course, from Beer's law it ought to be 0·03 mm. In the case of the $N/2$-solution, therefore, less light is absorbed than would be expected from Beer's law, because a greater thickness of that solution is necessary to produce a given absorption than that calculated from Beer's law. With increasing concentrations the divergence from Beer's law is still further marked, and in the case of the pure substance this divergence is very great indeed.

The complete set of observations are contained in table I, in which the first column contains the molecular concentration of the material. The second column shows the actual observed thicknesses through which the light of the absorption band is just transmitted, and in the third column are the thicknesses calculated from Beer's law. In the fourth column are shown the differences between the observed and calculated values, whilst the fifth column contains the ratios of these differences to the calculated thickness.

The greatest concentration obtainable, of course, was the pure substance itself, which was approximately 7·923*N*. On attempting to examine a still greater dilution than *N*/2000 in alcohol, it was found impossible to obtain accurate measurements owing to the fact that with the long length then necessary the absorption exerted by the alcohol came into play.

This, however, does not hold good in the case of water, because pure distilled water is quite diactinic up to very long lengths. We therefore investigated aqueous solutions of ethyl acetoacetate, starting with the most concentrated solution which could conveniently be managed in this solvent, which was *N*/20. It was noticed at once that the absorptive power of the aqueous solution is very much less than that of the alcohol solution of the same concentration, but this, of course, does not prevent any comparisons being made between any set of observations taken with the same solution. In table II are shown the results obtained with some aqueous solutions of ethyl acetoacetate, and it will be seen that in the case of the first two, Beer's law holds good. In the case of the *N*/500-solution the absorption is distinctly less than Beer's law would lead us to expect, and in the case of the *N*/1000-solution the selective absorption has entirely disappeared.

These results seem to us to be of considerable interest, for, although the same solvent has not been used throughout, it is quite evident that, starting from the pure substance, an increase in the amount of solvent present first of all causes a progressive increase in the amount of light absorbed until a constant maximum is reached. Further dilution then causes a decrease in the absorption, which is followed by an entire disappearance of the selective absorption.

Inasmuch as this result is exactly that prophesied by the general theory advanced above, we feel that it may be regarded as affording very great support to the theory.

In case it may be urged that the disappearance of the selective absorption in the case of the aqueous solution is due to the ionisation of the ester, it may be pointed out that a *N*/1000-solution in water at which the concentration of the selective absorption has disappeared, only about 0·1 per cent. of the ester is ionised.

We have also examined pyridine, and find somewhat similar results, although we have not yet been able to reach the dilution at which the pyridine ceases selectively to absorb light. In table III are shown the results given by pyridine, water being used as a solvent. From this statement it will be seen that a constant maximum is not reached before $N/50$-concentration, and that the deviation from Beer's law with greater concentrations is even more strikingly marked than in the case of ethyl acetoacetate. The first set of observations in the table refer to pure pyridine, which is about 12·4$N$. It may be pointed out that pyridine exhibits a very well-marked and deep absorption band, and the thicknesses given in table III refer to those thicknesses through which the rays of light correspond with the absorption band are just transmitted, that is, they refer to those thicknesses at which the head of the absorption band is observed.

We would draw attention to the fact that we find some divergence between our observations and some given by Purvis; for example, Purvis (T., 1910, **97**, 1546) states that no selective absorption is shown by films of aniline, even when the thickness is reduced to 0·001 mm. We find, however, clear evidence of the well-known absorption band, which, indeed, extends over a range of 0·015 to 0·009 mm.

It seems only reasonable to conclude from this that the thicknesses which Purvis gives in his papers are wrong. We would

### Table I.

*Ethyl Acetoacetate and Alcohol.*

| Normality. | Observed thickness. | Calculated thickness, *a*. | Difference, obs.—calc., *b*. | *b*/*a*. |
|---|---|---|---|---|
| | mm. | mm. | mm. | |
| 7·923 | 0·016 | 0·001893 | 0·015107 | 7·4 |
| 5·0 | 0·020 | 0·003 | 0·017 | 5·7 |
| 2·0 | 0·028 | 0·0075 | 0·0205 | 2·7 |
| 1·0 | 0·037 | 0·015 | 0·022 | 1·5 |
| 0·5 | 0·05 | 0·03 | 0·02 | 0·67 |
| 0·1 | 0·15 | 0·15 | 0 | 0 |
| 0·05 | 0·3 | 0·3 | 0 | 0 |
| 0·005 | 3·0 | 3·0 | 0 | 0 |
| 0·0025 | 6·0 | 6·0 | 0 | 0 |
| 0·00125 | 12·0 | 12·0 | 0 | 0 |
| 0·001 | 15·0 | 15·0 | 0 | 0 |
| 0·0005 | 30·0 | 30·0 | 0 | 0 |

### Table II.

*Ethyl Acetoacetate and Water.*

| Normality. | Observed thickness. | Calculated thickness, *a*. | Difference, obs.—calc., *b*. | *b*/*a*. |
|---|---|---|---|---|
| | mm. | mm. | mm. | |
| 0·05 | 6 | 6 | 0 | 0 |
| 0·025 | 12 | 12 | 0 | 0 |
| 0·01 | 25 | 30 | −5 | −0·17 |
| 0·002 | 120 | 150 | −30 | −0·2 |
| 0·001 | Selective absorption ceased | | | |

TABLE III.

*Pyridine and Water.*

| Normality. | Observed thickness. | Calculated thickness, *a*. | Difference, obs.—calc. *b*. | *b*/*a*. |
|---|---|---|---|---|
| | mm. | mm. | mm. | |
| 12·4 | 0·010 | 0·00064 | 0·00936 | 14·7 |
| 10·0 | 0·011 | 0·0008 | 0·0102 | 12·7 |
| 7·0 | 0·013 | 0·00114 | 0·01186 | 10·4 |
| 5·0 | 0·014 | 0·0016 | 0·0124 | 7·7 |
| 4·0 | 0·015 | 0·002 | 0·0130 | 6·5 |
| 2·0 | 0·019 | 0·004 | 0·015 | 3·7 |
| 1·0 | 0·024 | 0·008 | 0·016 | 2·0 |
| 0·2 | 0·067 | 0·04 | 0·027 | 0·67 |
| 0·02 | 0·40 | 0·40 | 0 | 0 |
| 0·002 | 4·0 | 4·0 | 0 | 0 |
| 0·0002 | 40·0 | 40·0 | 0 | 0 |

suggest that the mounting of the quartz plates in his cell is not sufficiently rigid to stand the strain produced by surface tension of the very thin films. If this were so when the plates are brought close together with a thin film of liquid in between them, the readings given by the instrument are very much smaller than the real thickness of the film owing to the fact that the plates have been forced apart by the surface tension. We would point out that if our instrument, even much more rigid though it be than that used by Purvis, is subject to the same error in a less degree, then such an error would tend to decrease the deviation that we have observed from Beer's law. In other words, if our readings are subject to a correction from this cause, such a correction would increase the deviations which we have observed.

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# XIV.—*The Constitution of Cytisine, the Alkaloid of Cytisus Laburnum. Part I. The Synthesis of a-Cytisolidine and of β-Cytisolidine.**

By ARTHUR JAMES EWINS.

CYTISINE, the poisonous alkaloid of the common laburnum (*Cytisus laburnum*), was first isolated in a pure state by Husemann and Marmé (*Zeitsch. f. Chem.*, 1865, **1**, 161), who gave it the formula $C_{20}H_{27}ON_3$. Partheil (*Ber.*, 1890, **23**, 3201), however, showed the true composition of the alkaloid to be $C_{11}H_{14}ON_2$, and this formula was confirmed by Buchka and Magelhaës (*Ber.*, 1891, **24**, 273, 674), as well as by subsequent workers.

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* This communication forms part of an investigation which is being carried out in collaboration with Dr. G. Barger.

The alkaloid is present in many other plants, for example, in other kinds of cytisus and in *Ulex europaeus*, the common gorse, the "ulexine" of which, isolated by Gerrard (*Ber.*, 1886, **19**, 838), was shown by Partheil and others to be identical with cytisine.

The interest attaching to this alkaloid has been very considerably increased by the recent work of Dale and Laidlaw (*J. Pharm. Expt. Ther.*, 1912, **3**, 205), who have shown that its physiological action is in all respects qualitatively and almost quantitatively indistinguishable from that of the very poisonous alkaloid nicotine. The question of its chemical constitution accordingly becomes of interest in so far as one might perhaps expect some chemical relationship with that of the latter alkaloid.

The chemical constitution of cytisine has previously been worked at chiefly by two investigators: Partheil (*loc. cit.*), and more especially by M. Freund and his co-workers (*Ber.*, 1901, **34**, 615; 1904, **37**, 16; 1906, **39**, 814). To the latter the following main facts with regard to the alkaloid are due. On treatment with hydriodic acid and phosphorus at a high temperature (230°) the alkaloid is decomposed, yielding as the main products of the reaction the following substances:

(*a*) Cytisoline, $C_{11}H_{11}ON$, a feebly basic, crystalline solid, melting when pure at 198°.

(*b*) β-Cytisolidine, $C_{11}H_{15}N$ (Freund), a basic oil, yielding a crystalline picrate (m. p. 229°) and platinichloride (m. p. 234°).

(*c*) A mixture of hydrocarbons melting at 185—230°.

(*d*) Ammonia.

Of these products, cytisoline on reduction with sodium and alcohol gives a base, α-cytisolidine, $C_{11}H_{15}N$, considered by Freund to be isomeric with β-cytisolidine. This base yielded an oily picrate and a crystalline platinichloride melting at 216°. Further, cytisoline on oxidation with chromic acid gives an acid, cytisolinic acid, $C_{10}H_8ON(CO_2H)$, obviously by oxidation of a methyl group in the molecule.

Lastly, Freund (*Ber.*, 1904, **37**, 16; 1906, **39**, 814) showed that on electrolytic reduction, cytisine, $C_{11}H_{14}ON_2$, was converted into a base, tetrahydrodeoxycytisine, $C_{11}H_{20}N_2$. Experiments soon showed that the main hope of gaining any further knowledge of the constitution of the alkaloid lay in the elucidation of the constitution of the products obtained by Freund by the action of hydriodic acid. Many attempts were made to obtain some product of oxidation from cytisine which would throw some light on the problem of its constitution. Cytisine is very readily attacked by oxidising agents, such as potassium permanganate and chromic acid, but, however the conditions of oxidation were varied, no pure product could be isolated except oxalic acid.

Equally disappointing were the attempts which were made to decompose the alkaloid by the action of acids or alkalis at high temperatures. Towards these reagents cytisine is stable to a remarkable degree. After heating with concentrated or dilute sulphuric or hydrochloric acids to temperatures of from 200° to 250°, or higher, for some time, the greater part of the alkaloid was recovered unchanged. Only with a saturated solution of hydrogen bromide in acetic acid, at a temperature of 250°, was there any indication of the formation of a new crystalline derivative, and even in this case the yield was extremely small. These experiments were consequently abandoned.

In repeating the experiments of Freund it was noticed that the base α-cytisolidine, obtained by the reduction of cytisoline by the action of sodium in alcohol, when dissolved in sulphuric acid and treated with a drop of nitric acid, gave a carmine-red colour shading to blue at the edge of the liquid. This reaction is somewhat similar to that given by tetrahydroquinoline, and it was considered probable that α-cytisolidine might be a substituted tetrahydroquinoline. Freund himself had considered the possibility of its being 1:8-dimethyltetrahydroquinoline, but synthesis of the latter compound had shown that this was not the case (*Ber.*, 1904, **37**, 22). The absence of a methyl group attached to the nitrogen atom of the base was easily shown, since a determination carried out according to the method of Herzig and Meyer for such a grouping gave a negative result. Moreover, since cytisoline has been shown to contain a methyl group, it follows that α-cytisolidine must be a dimethyltetrahydroquinoline if it is indeed a derivative of tetrahydroquinoline, and cytisoline a hydroxydimethylquinoline. The general properties of cytisoline gave considerable support to the above hypothesis when compared with those of the corresponding hydroxyquinolines already described in the literature. Like these derivatives, cytisoline is a feeble base. Its salts are dissociated by water, it gives a brownish-red coloration with ferric chloride solution, and on reduction it loses oxygen, taking up four atoms of hydrogen to give a base volatile in steam.

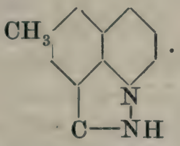
Excluding the bases containing a methyl group attached to the nitrogen atom, there are possible twenty-one isomeric dimethyltetrahydroquinolines. Of these, some ten are mentioned in the literature, but few of these are by any means well characterised. The task of identifying the base was therefore no light one. The synthesis of what were considered to be the more likely of these dimethyltetrahydroquinolines was commenced in collaboration with Mr. H. King, and some of the results of this work are described in the succeeding paper (Ewins and King, p. 104).

The work carried out in this direction unexpectedly threw a further light on the relationship of α-cytisolidine to β-cytisolidine, the basic oil obtained by the action of hydriodic acid on cytisine. The last-mentioned authors found a well-marked and fairly constant difference in the properties of the dimethyltetrahydroquinolines and the corresponding dimethylquinolines, chiefly in the melting points and solubilities of their salts. A similar relationship was observed to exist between the α- and β-cytisolidines, and a closer examination and analysis showed that the latter possessed the composition $C_{11}H_{11}N$, and not $C_{11}H_{15}N$, as stated by Freund (*loc. cit.*). It was therefore very probable that α-cytisolidine was the dimethyltetrahydroquinoline corresponding with the dimethylquinoline, β-cytisolidine, a relationship which was readily confirmed, β-cytisolidine on reduction with sodium in alcoholic solution giving a base identical with α-cytisolidine.

The problem thus resolved itself into the identification of β-cytisolidine as (probably) a dimethylquinoline. Here, again, there are twenty-one possible isomerides, of which about a dozen have been described, but again for the most part very imperfectly.

Finally, after a number of these dimethylquinolines had been prepared, the synthesis of 6:8-dimethylquinoline from *m*-4-xylidine was carried out. The base so obtained proved to be identical with β-cytisolidine, and on reduction yielded another base identical with α-cytisolidine. The constitution of these two bases is thus established beyond doubt. Further, cytisoline must be a corresponding hydroxydimethylquinoline. This is confirmed by the fact that on distillation with zinc dust β-cytisolidine is obtained. The position of the hydroxy-group is, however, as yet undetermined; but it is most probably either in the 3- or 4-position, since 2-hydroxy-6:8-dimethylquinoline prepared by the action of hypochlorous acid on 6:8-dimethylquinoline, although agreeing closely in general properties with cytisoline, was found to be different. 5-Hydroxy-6:8-dimethylquinoline was also synthesised, but the properties of this substance differ considerably from cytisoline, owing to the phenolic character of the hydroxy-group, for which reason also 7-hydroxy-6:8-dimethylquinoline may most probably be eliminated. Experiments to determine the constitution of cytisoline are in progress.

The constitution of cytisine itself still remains an open question. It is to be noticed, however, that cytisoline, $C_{11}H_{11}ON$, which, from the results recorded in this communication, must be a hydroxydimethylquinoline, is formed from cytisine by the loss of the elements of ammonia alone. The manner in which this elimination takes place is at present quite unknown. The most simple explanation is perhaps that cytisine is formed by the fusion of three rings (benzene, pyridine, and pyrazole rings), somewhat according to the following scheme:



Such a compound might conceivably lose ammonia under the conditions described, to yield dimethylquinoline derivatives; but there is so far no direct evidence in support of such a structure.

## EXPERIMENTAL.

### *The Action of Hydriodic Acid and Phosphorus on Cytisine.*

The method employed by Freund (*Ber.*, 1904, **37**, 16) to obtain cytisoline was as follows: Two grams of cytisine, 1 gram of red phosphorus, and 10 c.c. of hydriodic acid (D 1·7) were heated in sealed tubes for four hours at 225—230°. In this way 5 grams of cytisoline were obtained from 40 grams of cytisine. Experiment confirmed these results, but a slight modification was adopted by which the yield was somewhat increased. This consisted in heating 2 grams of cytisine, 0·4 gram of phosphorus, and 4 c.c. only of hydriodic acid to 230—235° for three hours. In this way, an average yield of 3·5 grams of cytisoline (m. p. 180°) was obtained from 20 grams of cytisine. At a slightly lower temperature a somewhat less pure product was obtained consisting of cytisoline, together with a substance or substances possessing very similar properties which render purification a matter of considerable difficulty. The reaction product was treated in a manner somewhat different from that employed by Freund. The contents of the tubes were poured into water, and on keeping the crystalline cytisoline separated out and was collected. The acid filtrate, on neutralisation, yielded a further small quantity of cytisoline. The solution was finally rendered alkaline with sodium hydroxide and distilled in a current of steam, when β-cytisolidine, together with a little α-cytisolidine, passed over. The yield of the base was small. From the residue in the distilling flask a considerable amount of unchanged cytisine could be recovered by extraction with chloroform.

### *The Formation of β-Cytisolidine from Cytisoline by Distillation with Zinc Dust.*

Four grams of cytisoline were distilled over zinc dust and zinc pumice in a current of hydrogen at a dull red heat. The red, oily distillate was dissolved in dilute (5 per cent.) hydrochloric acid, and the filtered acid solution extracted with ether. The small amount of extracted material was discarded. The aqueous solution was then rendered alkaline with sodium hydroxide, and again extracted with ether. The ethereal solution was washed with water, dried over anhydrous potassium carbonate, and the ether evaporated. The residue was distilled, and 0·9 gram of a colourless, limpid oil boiling at 132—133°/14 mm. was obtained. This base was easily shown to be identical with β-cytisolidine by comparison of its salts. The identity is shown in the following table:

| | Base from cytisoline. | β-Cytisolidine. |
|---|---|---|
| Picrate.................. | 224° | 224—225° (Freund 229°) |
| Platinichloride ...... | 234—235 | 234—235 |
| Nitro-derivative...... | 104 | 104—105 |

The melting points of mixtures in all these cases showed no depression.

### *The Synthesis of β-Cytisolidine* (6:8-*Dimethylquinoline*).

6:8-Dimethylquinoline was originally obtained by Leeds (*Ber.*, 1873, **16**, 289) by the dry distillation of xylidineacrolein, and was by him termed kryptidin. It was then obtained by Berend (*Ber.*, 1874, **17**, 2716) from *m*-4-xylidine by the Skraup synthesis.

For the preparation of the base the latter method was employed. Ten grams of *m*-4-xylidine, 5 grams of nitrobenzene, and 24 grams of glycerol were heated together in a large flask on a sand-bath, and 20 grams of concentrated sulphuric acid were gradually run through a dropping funnel into the heated mixture. In this way the reaction proceeded quite smoothly. The product was worked up in the usual manner, and 6·5 grams of a base boiling at 133—134°/14 mm. were obtained. (Found, C=83·9; H=7·1. Calc., C=84·0; H=7·0 per cent.)

The identity of this base with cytisolidine is shown by the following table:

| | 6:8-Dimethylquinoline. | β-Cytisolidine. |
|---|---|---|
| Boiling point ............ | 133—134°/14 mm. | 132—133°/14 mm. |
| Picrate...................... | 221—224 | 224—225 (Freund 229°) |
| Platinichloride ......... | 234—235 | 234—235 |
| Hydrochloride ......... | 246 | 250—260 |
| Nitro-derivative......... | 105 | 104—105 |

Mixed melting points in all cases showed no depression.

The formula $C_{11}H_{15}N$ assigned by Freund (*loc. cit.*) to β-cytisolidine was thus shown to be inaccurate. A specimen of β-cytisolidine picrate melting at 224—225°, obtained from cytisine by the action of hydriodic acid, was analysed with the following result:

0·1038 gave 0·2024 $CO_2$ and 0·0354 $H_2O$. C=53·2; H=3·8.
$C_{11}H_{11}N,C_6H_3O_7N_3$ requires C=52·8; H=3·6 per cent.

## *The Synthesis of α-Cytisolidine* (6:8-*Dimethyl*-1:2:3:4-*tetrahydroquinoline*).

Three grams of 6:8-dimethylquinoline were reduced in alcoholic solution with 5 grams of sodium. The mixture was diluted with water, the alcohol evaporated off, and the residue distilled in a current of steam. The distillate was extracted with ether, the ethereal solution washed and dried in the usual way, and the residue after evaporation of the ether distilled under diminished pressure. There were thus obtained 2·1 grams of a liquid boiling at 137°/11 mm.:

0·1582 gave 0·4746 $CO_2$ and 0·1328 $H_2O$. C=81·8; H=9·3.
$C_{11}H_{15}N$ requires C=82·0; H=9·3 per cent.

This was proved to be identical with α-cytisolidine by the preparation of a number of salts and derivatives, as shown by the following table:

| | 6:8-Dimethyl-1:2:3:4-tetrahydroquinoline. | α-Cytisolidine. | |
|---|---|---|---|
| | | Freund. | Ewins. |
| Boiling point ................... | 137°/11 mm. | — | 141—142°/14 mm. |
| Picrate ........ .................. | 147—148 | oily | 146 |
| Platinichloride.................. | 214—215 | 216° | 214—215 |
| Iodide of methyl derivative.. | 166 | — | 164—165 |
| Benzoyl derivative ............ | 103 | — | 103 |

Melting points of mixtures in all cases showed no depression.

Since 6:8-*dimethyl*-1:2:3:4-*tetrahydroquinoline* has not previously been synthesised, a more detailed account of its salts and derivatives follows.

The *picrate* is best prepared by the addition of an ethereal solution of picric acid to an ethereal solution of the base. The salt is not immediately precipitated, but on addition of light petroleum and rubbing with a glass rod, a gummy, reddish-yellow solid separates, which gradually hardens, and can then be collected. It is best crystallised from benzene by careful addition of light petroleum, when it separates in large, orange-yellow, rhombic plates, melting at 147—148°.

In the presence of water this salt shows a very great tendency to separate as an oil. Freund's failure to crystallise this salt is probably explained by this fact.

The *benzoyl* derivative is readily prepared by the Schotten-Baumann reaction, and crystallises from dilute alcohol in prisms melting at 103°:

0·1468 gave 0·4358 $CO_2$ and 0·0922 $H_2O$. C=81·0; H=7·0.

$C_{18}H_{19}ON$ requires C=81·5; H=7·2 per cent.

### 1:6:8-*Trimethyl*-1:2:3:4-*tetrahydroquinoline Hydriodide.*

This salt is produced by the addition of one molecule of methyl iodide to 6:8-dimethyl-1:2:3:4-tetrahydroquinoline.

6:8-Dimethyl-1:2:3:4-tetrahydroquinoline (0·4 gram) was boiled for a few minutes with a slight excess of methyl iodide. The solution was evaporated to dryness, the residue dissolved in a little methyl alcohol, and dry ether added, just insufficient to produce a precipitate. On keeping, crystals of the above salt separated out. They formed prisms melting at 164—165° (0·26 gram):

0·1242 gave 0·2156 $CO_2$ and 0·0638 $H_2O$. C=47·4; H=5·7.

$C_{12}H_{17}N,HI$ requires C=47·5; H=5·9 per cent.

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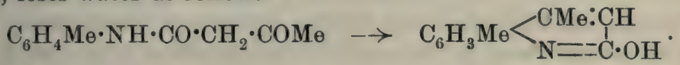
## XV.—*The Synthesis of Some New Dimethyltetrahydroquinolines.*

By ARTHUR JAMES EWINS and HAROLD KING.

IN the course of an investigation which is being carried out by one of us in conjunction with Dr. G. Barger, it became necessary for the purpose of comparison to prepare certain hydroxydimethylquinolines and their reduction products. Reference to the literature showed that a number of such substituted hydroxyquinolines had already been prepared, chiefly by Knorr (*Ber.*, 1884, **17**, 542; *Annalen*, 1889, **245**, 358) and Conrad and Limpach (*Ber.*, 1888, **21**, 525).

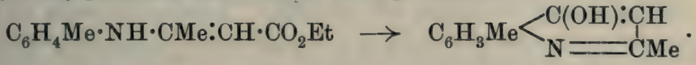
In the first place, we attempted the preparation of 2-hydroxy-4:8-dimethylquinoline by Knorr's method. This consists in heating molecular proportions of *o*-toluidine and ethyl acetoacetate in sealed tubes at 150—160° for several hours, and subsequently treating the crude product with cold concentrated sulphuric acid. On pouring into water, the hydroxyquinoline is precipitated. The method, however, gave very unsatisfactory results, a poor yield of an obviously very impure product being obtained. We subsequently found that the product described by Knorr as 2-hydroxy-4:8-dimethylquinoline must also have been very impure, since he gives for this compound a melting point of 185°, whereas we find that the pure substance melts at 217°.

The formation of a hydroxyquinoline by the above process depends on the production of the toluidide of acetoacetic acid, which then, under the dehydrating action of concentrated sulphuric acid, loses water as follows:



$$C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot COMe \longrightarrow C_6H_3Me{<}\begin{array}{l}CMe{:}CH\\ N{=}{=}C\cdot OH\end{array}.$$

The intermediate toluidide was not isolated by Knorr. Pawlewski (*Ber.*, 1889, **22**, 2203), however, described a substance obtained from the product, which he considered to be β-tolyliminocrotonic acid (isomeric with the toluidide), in accordance with Knorr's original view (*Ber.*, 1884, **17**, 542) that condensation took place, not as indicated above, but according to the following scheme, whereby 4-hydroxyquinoline derivatives were produced:



$$C_6H_4Me\cdot NH\cdot CMe{:}CH\cdot CO_2Et \longrightarrow C_6H_3Me{<}\begin{array}{l}C(OH){:}CH\\ N{=}{=}{=}CMe\end{array}.$$

Knorr, however, had already corrected his original interpretation of the reaction, and Pawlewski's substance was in all probability, from its melting point and the analytical figures, the *o*-toluidide of acetoacetic acid. The 4-hydroxyquinolines were afterwards synthesised by Conrad and Limpach from the β-toluidinocrotonic esters obtained by the interaction of the substances in the cold (*Ber.*, 1888, **21**, 525).

As we required considerable quantities of these hydroxyquinolines for our purpose, we experimented with the object of obtaining the required toluidides in a state of purity and improved yield. After several attempts we found that by simply boiling together molecular proportions of the necessary toluidine and ethyl acetoacetate for a very short time (one to one and a-half minutes) the product solidified on cooling to a mass of crystals, which, after recrystallisation, were obtained pure in good yield, averaging 55 per cent. of the theoretical.* The toluidides so obtained are readily and almost quantitatively converted into the corresponding hydroxyquinolines (carbostyrils) by heating at 100° for ten to fifteen minutes with concentrated sulphuric acid. On pouring into water, the hydroxyquinolines separate out immediately in an almost pure condition.

The hydroxyquinolines so obtained on reduction with sodium and alcohol are converted mainly into the corresponding tetrahydroquinolines. There are indications of the formation of intermediate products, possibly hydroxydihydroquinolines, but this has not so far been investigated. On distillation with zinc dust, the hydroxyquinolines are converted into dimethylquinolines (Knorr, *Annalen*, 1889, **245**, 358). The reduction, however, takes place only with some difficulty, a rather high temperature and a current of hydrogen being essential in order to obtain a satisfactory yield of base. The characterisation of these dimethylquinolines as at present recorded is very unsatisfactory and incomplete. We have accordingly redetermined the boiling points of these bases, and place on record some of their more characteristic salts and derivatives.

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* The preparation of the anilide of ethyl acetoacetate can be readily carried out in a precisely similar manner.

The new dimethyltetrahydroquinolines described in this communication are readily distinguished from the corresponding dimethylquinolines by the following properties. Whilst the dimethylquinolines give no coloration when dissolved in sulphuric acid (the solution, however, shows a marked blue fluorescence) and treated with a drop of nitric acid, with the tetrahydro-derivatives well-marked colour reactions are obtained. Again, the salts of the tetrahydro-bases generally melt at a considerably lower temperature than those of the dimethylquinolines, the picrates, for example, differing by about 60—-70°. The picrates of the tetrahydro-bases are orange or orange-yellow salts, moderately soluble in water, and very readily so in acetone. Those of the dimethylquinolines are pale yellow, and very sparingly soluble in hot water or alcohol. The tetrahydro-bases also yield characteristic benzoyl derivatives of low melting point by the Schotten-Baumann reaction.

## EXPERIMENTAL.

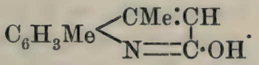
*Acetoaceto-o-toluidide*, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4Me$.

A mixture of 30 grams of ethyl acetoacetate and 24 grams of *o*-toluidine was rapidly heated to boiling, and the liquid kept vigorously boiling for one to one and a-half minutes. The cooled product set to a mass of crystals, which were collected and recrystallised from ethyl acetate, when short, rectangular prisms (25 grams) melting at 107—108° were obtained:

0·1562 gave 0·3943 $CO_2$ and 0·1008 $H_2O$. C=68·8; H=7·2.
0·1950 ,, 12·5 c.c. $N_2$ (moist) at 10° and 760 mm. N=7·6.
$C_{11}H_{13}O_2N$ requires C=69·1; H=6·8; N=7·3 per cent.

We were also able to isolate a certain amount of this toluidide from the reaction product obtained by Knorr's method (heating to 150—160° in sealed tubes), and it is most probable that the substance isolated by Pawlewski (*Ber.*, 1889, **22**, 2203) from this reaction product, and considered by him to be *o*-tolyliminocrotonic acid (m. p. 111—112°), was, in fact, acetoaceto-*o*-toluidide. Since, however, no details of the method of isolation or of the properties of the substance are given, it is not possible to determine this point except by synthesis of the acid. That the toluidide possesses the constitution assigned to it by the present authors is obvious from the fact that the product is insoluble in sodium carbonate, showing the absence of the carboxyl group, and that the alcoholic solution gives with ferric chloride a purple coloration indicative of the enolic form of the acetoacetic grouping which could hardly be the case if the substituting toluidine were in the position assigned to it by Pawlewski. Its constitution further follows from its ready conversion into 2-hydroxy-4:8-dimethylquinoline by the action of dehydrating agents, whereas the acid described by Pawlewski would be expected to give the isomeric 4-hydroxy-2:8-dimethylquinoline obtained by Conrad and Limpach by another method.

*2-Hydroxy-4:8-dimethylquinoline*,



$\mathrm{C_6H_3Me}\Big\langle\begin{array}{l}\mathrm{CMe{:}CH}\\ \mathrm{N{=\!=}C{\cdot}OH}\end{array}.$

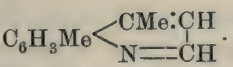
Acetoaceto-*o*-toluidide (19 grams) was dissolved in concentrated sulphuric acid (20 c.c.), and the mixture heated in the boiling-water bath for fifteen minutes. The product was then poured into about ten volumes of water, when a white, crystalline solid separated. After some time this was collected, and recrystallised from dilute acetic acid, when it separated in long, thin plates, melting at 217—218°:

0·1180 gave 0·3310 $CO_2$ and 0·0628 $H_2O$. C = 76·5; H = 5·9.

$C_{11}H_{11}ON$ requires C = 76·3; H = 6·3 per cent.

This carbostyril was originally described by Knorr (*Ber.*, 1884, **17**, 542), who obtained it in a very impure form, melting at 185° from the crude product obtained as described. The substance is a weak base, very sparingly soluble in cold water, more readily so in hot. It forms salts with concentrated mineral acids, but these are decomposed by excess of water with liberation of the crystalline base. On distillation with zinc dust it yields 4:8-dimethylquinoline, and on reduction by sodium and alcohol, 4:8-dimethyl-1:2:3:4-tetrahydroquinoline.

*4:8-Dimethylquinoline*,



$\mathrm{C_6H_3Me}\Big\langle\begin{array}{l}\mathrm{CMe{:}CH}\\ \mathrm{N{=\!=}CH}\end{array}.$

This base was originally described by Knorr as a pungent oil boiling at 273—274°/751 mm. It is obtained by distilling

2-hydroxy-4:8-dimethylquinoline over zinc dust in a current of hydrogen. In order to purify the base it was converted into the pure picrate described below. The salt so obtained was treated with a concentrated solution of potassium hydroxide, and distilled in a current of steam. The oily liquid was extracted from the distillate by means of ether, and, after drying and removal of the solvent, distilled. The base was an almost colourless, limpid oil, boiling at 134—135°/12 mm. and 258—259°/758 mm., which on keeping solidified to a crystalline mass melting at 54—55°. (Found, C=83·5; H=7·0. $C_{11}H_{11}N$ requires C=84·0; H=7·0 per cent.)

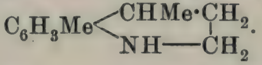
4:8-*Dimethylquinoline picrate* was obtained by precipitating the ethereal solution of the base by an ethereal solution of picric acid. The salt was recrystallised from dilute alcohol, and was obtained in lemon-yellow, rhombic prisms, melting at 216—217°:

0·1821 gave 0·3506 $CO_2$ and 0·0582 $H_2O$. C=52·6; H=3.5.
$C_{11}H_{11}N,C_6H_3O_7N_3$ requires C=52·8; H=3·6 per cent.

The salt is very sparingly soluble in hot water or alcohol, but rather more readily so in acetone.

The *platinichloride* crystallises from dilute alcohol in buff-coloured needles, melting and decomposing at 226—227° (Knorr gives 220°).

### 4:8-*Dimethyl*-1:2:3:4-*tetrahydroquinoline*,



$$C_6H_3Me\left\langle\begin{array}{l}CHMe\cdot CH_2\\ NH—CH_2\end{array}\right.$$

2-Hydroxy-4:8-dimethylquinoline (7·5 grams) was reduced by sodium (15 grams) in concentrated absolute alcoholic solution. The solution was diluted with an equal volume of water, the alcohol distilled off, and the residue distilled in a current of steam. The oily liquid which passed over was extracted with ether, the ethereal solution dried over potassium carbonate, and after evaporating off the ether the residue was fractionally distilled. The distillate was converted into the picrate, which was obtained pure by recrystallising from dilute alcohol. The regenerated base then boiled at 133—134°/16 mm. and at 256—258°/750 mm.:

0·1566 gave 0·4708 $CO_2$ and 0·1322 $H_2O$. C=82·0; H=9·4.
$C_{11}H_{15}N$ requires C=82·0; H=9·3 per cent.

4:8-*Dimethyl*-1:2:3:4-*tetrahydroquinoline* is a colourless oil, very sparingly soluble in water, and easily volatile with steam. When treated with concentrated sulphuric acid and a drop of nitric acid a deep orange-red colour is produced.

The *picrate*, obtained in the usual manner, forms orange-yellow, rhombic prisms, melting at 160°. It is sparingly soluble in cold water, but fairly readily so in hot water, alcohol, or acetone:

0·1090 gave 0·2096 $CO_2$ and 0·0448 $H_2O$. C=52·4; H=4·6.

$C_{11}H_{15}N,C_6H_3O_7N_3$ requires C=52·3; H=4·6 per cent.

The *benzoyl* derivative, $C_{18}H_{19}ON$, prepared by the Schotten-Baumann reaction, crystallises from dilute alcohol in prisms melting at 104—105°.

### *Acetoaceto*-m-*toluidide*, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4Me$.

This compound is obtained by a method exactly similar to that employed in the preparation of the ortho-compound. On recrystallisation from benzene and light petroleum it separated in pearly leaflets melting at 57—58°:

0·1570 gave 0·3972 $CO_2$ and 0·0980 $H_2O$. C=69·0; H=6·93.

$C_{11}H_{13}O_2N$ requires C=69·1; H=6·8 per cent.

Its general properties are in all respects similar to those of the isomeric ortho-compound.

Owing to the low melting point of the solid, however, its separation from the crude product was found to be somewhat troublesome. In the preparation of the corresponding 2-hydroxy-4:7-dimethylquinoline, therefore, the crude product was directly treated with concentrated sulphuric acid at 100° for fifteen minutes, and the product poured into water. After crystallisation from dilute acetic acid a good yield (41 per cent.) of the hydroxyquinoline melting at 220° was readily obtained. From this the corresponding 4:7-dimethylquinoline and 4 : 7-dimethyl-1:2:3:4-tetrahydroquinoline were obtained by zinc dust distillation and reduction by sodium in alcohol respectively.

### 4:7-*Dimethylquinoline*, $C_{11}H_{11}N$.

2-Hydroxy-4:7-dimethylquinoline was distilled with zinc dust as described in the case of the corresponding 2-hydroxy-4:8-dimethylquinoline, and the product worked up as before. In this way from 10 grams of hydroxyquinoline were obtained 3·3 grams of a colourless oil. In order to obtain the pure base it was converted into the picrate, and the base regenerated from the pure salt boiled at 140—141°/15 mm.

The *picrate* was prepared in the manner described for the picrate of 4:8-dimethylquinoline, and was crystallised from dilute alcohol. It forms broad, rectangular, golden-yellow prisms, melting at 224°:

0·1736 gave 0·3374 $CO_2$ and 0·0566 $H_2O$. C=53·0; H=3·6.

$C_{11}H_{11}N,C_6H_3O_7N_3$ requires C=52·8; H=3·6 per cent.

This salt is very sparingly soluble in cold water, and only moderately so in hot water or alcohol.

### 4:7-*Dimethyl*-1:2:3:4-*tetrahydroquinoline.*

Ten grams of 2-hydroxy-4:7-dimethylquinoline were dissolved in boiling absolute alcohol, and 12 grams of sodium added to the boiling solution in small quantities at a time. The sodium salt of the hydroxyquinoline separates as a spongy mass, but slowly dissolves as the reduction proceeds. The dimethyltetrahydroquinoline was recovered as previously described. Yield, 5 grams.

The base was converted into the picrate, and recovered from the pure picrate by steam distillation from alkaline solution.

4:7-*Dimethyl*-1:2:3:4-*tetrahydroquinoline* is a colourless oil, which dissolves in concentrated sulphuric acid with a faint yellow colour, and on addition of a drop of concentrated nitric acid gives a purple-brown coloration. It boils at 136—138°/13 mm., and 268—270°/769 mm.:

0·1456 gave 0·4364 $CO_2$ and 0·1260 $H_2O$. C=81·8; H=9·3.

$C_{11}H_{15}N$ requires C=82·0; H=9·3 per cent.

The *picrate* crystallises from dilute alcohol in long, orange-yellow, serrated needles, melting at 155—156°. Its solubilities resemble those of the 4:8-dimethyltetrahydroquinoline picrate already described:

0·1420 gave 0·2728 $CO_2$ and 0·0598 $H_2O$. C=52·4; H=4·7.

$C_{11}H_{15}N,C_6H_3O_7N_3$ requires C=52·3; H=4·6 per cent.

The *benzoyl* derivative, $C_{18}H_{19}ON$, prepared by the Schotten-Baumann reaction, crystallises from light petroleum in bundles of leaflets, and melts at 84—85°.

### *Acetoaceto*-p-*toluidide*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$.

This compound was prepared in the same way as the toluidides already described, and was similar to them in general properties. After crystallisation from ethyl acetate it was obtained in well-formed prisms melting at 94—95°:

0·1356 gave 0·3442 $CO_2$ and 0·0844 $H_2O$. C=69·2; H=6·9.

$C_{11}H_{13}O_2N$ requires C=69·1; H=6·8 per cent.

The corresponding hydroxyquinoline (2-hydroxy-4:6-dimethylquinoline) was obtained by the action of concentrated sulphuric acid, as described before, and was found to agree in melting point and properties with the compound described by Knorr. It was submitted to distillation with zinc dust and reduction by sodium and alcohol, yielding 4:6-dimethyl- and 4:6-dimethyl-1:2:3:4-tetrahydro-quinolines respectively.

### 4:6-*Dimethylquinoline.*

Ten grams of 2-hydroxy-4:6-dimethylquinoline were distilled with zinc dust. The crude 4:6-dimethylquinoline so obtained was distilled, yielding 3·5 grams, which were converted into the picrate. The pure base was recovered from the purified picrate, and boiled at 140—141°/12 mm. and 255—256°/760 mm.

4:6-Dimethylquinoline picrate crystallises from dilute alcohol in long, rectangular prisms, melting at 236—237° (Knorr gives 230°). (Found, C=52·7; H=3·6. Calc., C=52·8; H=3·6 per cent.)

The solubilities are similar to the dimethylquinoline picrates already described.

### 4:6-*Dimethyl*-1:2:3:4-*tetrahydroquinoline.*

Ten grams of 2-hydroxy-4:6-dimethylquinoline were reduced in concentrated boiling alcoholic solution by 24 grams of sodium. The dimethyltetrahydroquinoline was recovered by steam distillation, and after distillation under diminished pressure yielded 4·3 grams of base.

The pure base was obtained from the purified picrolonate by steam distillation in alkaline solution. It boiled at 135—137°/15 mm. and 254—256°/750 mm.

4:6-*Dimethyl*-1:2:3:4-*tetrahydroquinoline* is a colourless oil. It dissolves in concentrated sulphuric acid with a deep purple colour, which slowly passes into blue, and finally becomes deep green:

0·1764 gave 0·5296 $CO_2$ and 0·1482 $H_2O$. C=81·9; H=9·4.

$C_{11}H_{15}N$ requires C=82·0; H=9·3 per cent.

The *picrolonate*, prepared in ethereal solution and crystallised from dilute alcohol, crystallises in hard, yellow rhombs, and melts at 204—205°. It is very sparingly soluble in boiling water or alcohol:

0·1494 gave 0·3252 $CO_2$ and 0·0732 $H_2O$. C=59·4; H=5·4.

$C_{11}H_{15}N,C_{10}H_8O_5N_4$ requires C=59·3; H=5·4 per cent.

The *picrate* is obtained as a gummy solid by precipitating the ethereal solution with light petroleum. It can be recrystallised from benzene, and separates in rectangular plates melting at 116—117°:

0·1162 gave 0·2234 $CO_2$ and 0·0494 $H_2O$. C=52·4; H=4·7.

$C_{11}H_{15}N,C_6H_3O_7N_3$ requires C=52·3; H=4·6 per cent.

The *benzoyl* derivative, prepared by the Schotten-Baumann reaction, crystallises from dilute alcohol in pearly leaflets melting at 109—110°:

0·1372 gave 0·4094 $CO_2$ and 0·0880 $H_2O$. C=81·4; H=7·1.

$C_{18}H_{19}ON$ requires C=81·5; H=7·2 per cent.

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# XVI.—*Optically Active Glycols Derived from the Phenyl-lactic Acids. Part I.*

By ALEX. MCKENZIE and GEOFFREY MARTIN.

IN a previous paper by McKenzie and Wren (T., 1910, **97**, 473) it was shown that *l*-triphenylethylene glycol, $OH\cdot CHPh\cdot CPh_2\cdot OH$, can be prepared by the action of magnesium phenyl bromide on *l*-benzoin or on methyl *l*-mandelate. The two latter compounds are related in configuration, since *l*-benzoin is prepared from the *l*-mandelamide corresponding with *l*-mandelic acid without the employment of any operation which involves the substitution of a grouping directly attached to the asymmetric atom. The above-mentioned glycol is nevertheless strongly dextrorotatory, the value for the specific rotatory power in acetone solution being $+221\cdot3°$, whereas *l*-benzoin has $[\alpha]_D$ $-118\cdot6°$ in the same solvent. In marked contrast is the rotation of *l*-$\alpha\beta$-dihydroxy-$\alpha$-phenyl*iso*butane, $OH\cdot CHPh\cdot CMe_2\cdot OH$ (derived from methyl *l*-mandelate), which has $[\alpha]_D$ $-21\cdot6°$ in acetone solution, the lævorotation accordingly persisting in this compound. On the other hand, the glycol,

$$OH\cdot CHPh\cdot CMePh\cdot OH,$$

derived from *l*-benzoin, is dextrorotatory, having $[\alpha]_D$ $+34°$.

The present paper contains a description of several glycols which have been prepared from the optically active phenyl-lactic acids, $C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H$ and $C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H$ (McKenzie and Humphries, T., 1910, **97**, 121; McKenzie and Wren, *ibid.*, 1355), by the application of the Grignard action. The acids possess almost identical rotatory powers in ethyl-alcoholic solution, namely, $[\alpha]_D$ $-18\cdot9°$ and $-18\cdot7°$ respectively for the *l*-acids. In aqueous solution their rotations are also not much different; *d*-$\alpha$-hydroxy-$\beta$-phenylpropionic acid has $[\alpha]_D$ $+22\cdot8°$, and for comparison we have determined the rotation of the *l*-$\beta$-hydroxy-acid in aqueous solution, and have found the value $[\alpha]_D$ $-21°$.

The glycols obtained from the *l*-$\beta$-hydroxy-acid gave the following values:

| | $[\alpha]_D$ in acetone solution. |
|---|---|
| $OH\cdot CHPh\cdot CH_2\cdot CPh_2\cdot OH$ .................. | $+3\cdot6°$ |
| $OH\cdot CHPh\cdot CH_2\cdot CMe_2\cdot OH$ .................. | $-57\cdot1$ |
| $OH\cdot CHPh\cdot CH_2\cdot C(CH_2Ph)_2\cdot OH$ ..... ...... | $-82\cdot8$ |

The depression in rotation caused by the displacement of methyl by phenyl groups is obvious in this series also, and is comparable with the effects observed by Rupe with the menthyl esters of various unsaturated acids. The influence, however, of the introduction of the methylene group between the $\cdot CPh_2\cdot OH$ group and the asymmetric centre is such as to cause the swing round of rotation to be less pronounced than in the case of triphenylethylene glycol.

The glycols derived from the α-hydroxy-acids gave the following values:

| | $[\alpha]_D$ in acetone solution. |
|---|---|
| *l*-$CH_2Ph{\cdot}CH(OH){\cdot}CPh_2{\cdot}OH$ .................. | $-109{\cdot}9°$ |
| *l*-$CH_2Ph{\cdot}CH(OH){\cdot}CMe_2{\cdot}OH$ .................. | $-70{\cdot}8$ |
| *d* $CH_2Ph{\cdot}CH(OH){\cdot}CEt_2{\cdot}OH$ .............. | $+58{\cdot}7$ |
| *d*-$CH_2Ph{\cdot}CH(OH){\cdot}C(CH_2Ph)_2{\cdot}OH$ ......... | $+7{\cdot}5$ |

The effect is thus reversed when the methylene group is interposed between the phenyl group and the asymmetric centre.

## EXPERIMENTAL.

### αγ-*Dihydroxy-ααγ-triphenylpropanes.*

In the preparation of the various Grignard reagents used in the course of the present research it was found to be very convenient to employ an excess of magnesium (from 2 to 4 atoms for each molecule of haloid). Not only is the action completed more quickly than by the usual method, but the formation of hydrocarbons according to the scheme $RMgX + XR = R{\cdot}R + MgX_2$ is also to a certain extent minimised. This modification was suggested by Schmidlin and Massini (*Ber.*, 1909, **42**, 2381).

The optically active β-hydroxy-β-phenylpropionic acids were prepared as described by McKenzie and Humphries (T., 1910, **97**, 121). An ethereal solution of the *d*-acid (3 grams) was gradually added to the Grignard reagent prepared from bromobenzene (38 grams) and magnesium (24 grams), and the mixture then heated for fifteen minutes. After decomposition in the usual manner with ice and sulphuric acid, the diphenyl was removed from the product by means of light petroleum, and the crude glycol (2·6 grams) was purified by crystallisation from ethyl alcohol. Yield, 1·7 grams.

d-αγ-*Dihydroxy-ααγ-triphenylpropane*, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}CPh_2{\cdot}OH$, separates from ethyl alcohol in colourless, rectangular crystals, and melts at 147—148°. It is very sparingly soluble in water. It dissolves readily in boiling light petroleum (b. p. 60—80°) or benzene, separating on cooling. It is readily soluble in acetone or ether. When added to concentrated sulphuric acid, it becomes scarlet, the solution being reddish-orange, and exhibiting slight fluorescence. For analysis it was dried at 100°:

0·1496 gave 0·4535 $CO_2$ and 0·0885 $H_2O$. C = 82·7; H = 6·6.

$C_{21}H_{20}O_2$ requires C = 82·9; H = 6·6 per cent.

The specific rotation was determined. In acetone solution:

$$l = 4,\ c = 1{\cdot}1368,\ \alpha_D^{16}\ -0{\cdot}14°,\ [\alpha]_D^{16}\ -3{\cdot}1°.$$

In benzene solution:

$l=4$, $c=1{\cdot}174$, $\alpha^{16}_{D}+0{\cdot}16^\circ$, $[\alpha]^{16}_{D}+3{\cdot}4^\circ$.

l-$\alpha\gamma$-*Dihydroxy-$\alpha\alpha\gamma$-triphenylpropane*, prepared from *l*-$\beta$-hydroxy-$\beta$-phenylpropionic acid, is similar in properties to its *d*-isomeride:

0·1156 gave 0·3498 $CO_2$ and 0·0681 $H_2O$. C=82·5; H=6·6.

$C_{21}H_{20}O_2$ requires C=82·9; H=6·6 per cent.

In acetone solution:

$l=4$, $c=2{\cdot}0828$, $\alpha^{15}_{D}+0{\cdot}30^\circ$, $[\alpha]^{15}_{D}+3{\cdot}6^\circ$.

In benzene solution:

$l=4$, $c=1{\cdot}1632$, $\alpha^{8}_{D}-0{\cdot}17^\circ$, $[\alpha]^{18}_{D}-3{\cdot}7^\circ$.

r-$\alpha\gamma$-*Dihydroxy-$\alpha\alpha\gamma$-triphenylpropane*, prepared from *r*-$\beta$-hydroxy-$\beta$-phenylpropionic acid, separates from benzene in colourless, rectangular crystals, and melts at 127—128°:

0·1837 gave 0·5564 $CO_2$ and 0·112 $H_2O$. C=82·6; H=6·8.

$C_{21}H_{20}O_2$ requires C=82·9; H=6·6 per cent.

This glycol may also be prepared conveniently by the interaction of magnesium phenyl bromide and *methyl* dl-$\beta$-*hydroxy*-$\beta$-*phenylpropionate*, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2Me$, a viscid oil, which boils at 158—161°/17—18 mm.:

0·2095 gave 0·509 $CO_2$ and 0·1285 $H_2O$. C=66·3; H=6·9.

$C_{10}H_{12}O_3$ requires C=66·6; H=6·7 per cent.

The three glycols described exhibit a strong green triboluminescence.* In quoting several cases where *d*- and *l*-modifications exhibited triboluminescence whereas the *r*-isomeride did not, Tschugaev (*Ber.*, 1901, **34**, 1820) suggests that there is possibly some connexion between this phenomenon and optical activity; such a connexion appears, however, to be unlikely.

### $\alpha\gamma$-*Dihydroxy-$\alpha$-phenyl*iso*pentanes.*

Attempts to obtain the *l*-glycol by the action of magnesium methyl iodide on the *l*-hydroxy-acid having failed, the active esters were prepared by the hydrogen chloride method from the active acids and methyl alcohol. Repeated distillation under diminished pressure should, however, be avoided, since partial racemisation apparently takes place somewhat readily under the influence of heat. The maximum rotation observed for the *d*-ester was $[\alpha]_D+17{\cdot}4^\circ$ for $c=4{\cdot}558$ in ethyl-alcoholic solution, and for the *l*-ester $[\alpha]_D-17{\cdot}0^\circ$ under similar conditions. Those values are probably correct for the optically pure esters, the *d*-acid (free from the *r*-isomeride) having been prepared from the *d*-ester with

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* The parent hydroxy-acids are also triboluminescent, although to a less degree than the glycols.

$[\alpha]_D$ + 17·4° by saponifying it at the ordinary temperature with aqueous alcoholic potassium hydroxide.

Six grams of methyl *d*-β-hydroxy-β-phenylpropionate were added gradually within ten minutes to an excess of magnesium methyl iodide prepared from 37 grams of methyl iodide, and the product was allowed to remain overnight before decomposition with ice and ammonium chloride. The crude material was purified by crystallisation from a mixture of benzene and light petroleum, when 4·7 grams of the glycol were obtained.

d-*αγ-Dihydroxy-α-phenyl*iso*pentane*, $OH\cdot CHPh\cdot CH_2\cdot CMe_2\cdot OH$, separates in colourless, silky, rectangular crystals, and melts at 70—71°. It is practically insoluble in water, sparingly soluble in light petroleum, and easily so in cold benzene, acetone, or ether. Its behaviour towards sulphuric acid is similar to that exhibited by the αγ-dihydroxy-ααγ-triphenylpropanes:

0·1368 gave 0·368 $CO_2$ and 0·1138 $H_2O$. C = 73·4; H = 9·3.

$C_{11}H_{16}O_2$ requires C = 73·3; H = 9·0 per cent.

Its rotation was determined in acetone solution:

$$l=2,\ c=4{\cdot}502,\ \alpha_D^{13}\ +5{\cdot}11^\circ,\ [\alpha]_D^{13}\ +56{\cdot}8^\circ.$$

In benzene solution:

$$l=2,\ c=3{\cdot}742,\ \alpha_D^{14}\ +5{\cdot}41^\circ,\ [\alpha]_D^{14}\ +72{\cdot}3^\circ$$

l-*αγ-Dihydroxy-α-phenyl*iso*pentane*, prepared from methyl *l*-β-hydroxy-β-phenylpropionate, melts at 70—71°:

0·148 gave 0·3975 $CO_2$ and 0·1192 $H_2O$. C = 73·2; H = 9·0.

$C_{11}H_{16}O_2$ requires C = 73·3; H = 9·0 per cent.

In acetone solution:

$$l=2,\ c=4{\cdot}746,\ \alpha_D^{13}\ -5{\cdot}42^\circ,\ [\alpha]_D^{13}\ -57{\cdot}1^\circ.$$

In benzene solution:

$$l=2,\ c=3{\cdot}676,\ \alpha_D^{13}\ -5{\cdot}32^\circ,\ [\alpha]_D^{13}\ -72{\cdot}3^\circ.$$

r-*αγ-Dihydroxy-α-phenyl*iso*pentane*, prepared from methyl *dl*-β-hydroxy-β-phenylpropionate, separates from light petroleum (b. p. 60—80°) in colourless, rectangular crystals. It may also be crystallised from ethyl alcohol:

0·216 gave 0·5806 $CO_2$ and 0·17 $H_2O$. C = 73·3; H = 8·8.

$C_{11}H_{16}O_2$ requires C = 73·3; H = 9·0 per cent.

No triboluminescence was observed with the isomeric αγ-dihydroxy-γ-phenyl-αα-dimethylpropanes.

### l-*βδ-Dihydroxy-αδ-diphenyl-β-benzyl*-n-*butane*.

An ethereal solution of 3 grams of methyl *l*-β-hydroxy-β-phenylpropionate was gradually added to the Grignard reagent prepared from 28 grams of benzyl chloride, and the mixture boiled for one hour. After decomposition of the additive product, the ether was distilled off, and the dibenzyl then removed by steam distillation. The residual resin was finally caused to solidify by covering it with *N*/10-aqueous potassium hydroxide containing a little ethyl alcohol, and allowing it to remain thus for three days. The glycol was purified by crystallisation from aqueous alcohol. Yield, 4·6 grams.

l-βδ-*Dihydroxy-αδ-diphenyl-β-benzyl*-n-*butane*,

$$OH{\cdot}CHPh{\cdot}CH_2{\cdot}C(Ph{\cdot}CH_2)_2{\cdot}OH,$$

separates from aqueous ethyl alcohol in colourless needles, and melts at 85—86°. It may also be crystallised from light petroleum, in which it is sparingly soluble at the ordinary temperature. It is very soluble in cold chloroform, benzene, or ethyl alcohol. It dissolves sparingly in cold concentrated sulphuric acid, the solution being yellow:

0·1344 gave 0·41 $CO_2$ and 0·0888 $H_2O$. C=83·2; H=7·4.

$C_{23}H_{24}O_2$ requires C=83·1; H=7·3 per cent.

In acetone solution:

$$l=2,\ c=3{\cdot}655,\ \alpha_D^{18}\ -6{\cdot}05°,\ [\alpha]_D^{18}\ -82{\cdot}8°.$$

In benzene solution:

$$l=2,\ c=3{\cdot}761,\ \alpha_D^{18}\ -6{\cdot}58°,\ [\alpha]_D^{18}\ -87{\cdot}5°.$$

In ethyl-alcoholic solution:

$$l=2,\ c=4{\cdot}463,\ \alpha_D^{16}\ -6{\cdot}67°,\ [\alpha]_D^{16}\ -74{\cdot}7°.$$

This glycol exhibited a feeble triboluminescence.

Attempts to prepare the ethyl, *o*-tolyl, and naphthyl glycols were unsuccessful, probably owing to the dehydrating effect of the Grignard reagents.

### l-αβ-*Dihydroxy-ααγ-triphenylpropane.*

*r*-α-Hydroxy-β-phenylpropionic acid was resolved into its optically active components according to the method of McKenzie and Wren (T., 1910, **97**, 1355).*

An ethereal solution of *l*-α-hydroxy-β-phenylpropionic acid (3 grams) was added to the Grignard reagent prepared from 38 grams of bromobenzene. The mixture was boiled for three hours. The crude glycol, obtained after removal of the diphenyl by distillation in steam, amounted to 4·1 grams, and was crystallised first from a mixture of benzene and light petroleum and then three times from light petroleum (b. p. 60—80°). Yield, 2·3 grams.

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* Ehrlich and Jacobsen (*Ber.*, 1911, **44**, 888) have made the interesting observation that *d*-α-hydroxy-β-phenylpropionic acid is produced by the growth of *Oidium lactis* on *r*-phenylalanine, the properties of the *d*-hydroxy-acid being in accordance with those described by McKenzie and Wren (*loc. cit.*).

l-*αβ-Dihydroxy-ααγ-triphenylpropane*, $CH_2Ph\cdot CH(OH)\cdot CPh_2\cdot OH$, separates in colourless, rectangular crystals, and melts at 96—97°. It is sparingly soluble in cold light petroleum, and easily so in benzene. When added to cold concentrated sulphuric acid, it becomes scarlet, and the solution is yellow to orange in tint:

0·1228 gave 0·3736 $CO_2$ and 0·0734 $H_2O$. C=83·0; H=6·7.

$C_{21}H_{20}O_2$ requires C=82·9; H=6·6 per cent.

In acetone solution:

$$l=2,\ c=2{\cdot}502,\ \alpha_D^{16\cdot5}\ -5{\cdot}50°,\ [\alpha]_D^{16\cdot5}\ -109{\cdot}9°.$$

In benzene solution:

$$l=2,\ c=2{\cdot}753,\ \alpha_D^{16}\ -7{\cdot}60°,\ [\alpha]_D^{16}\ -138{\cdot}0°.$$

This glycol exhibited a vivid triboluminescence.

### l-*βγ-Dihydroxy-α-phenyl*isopentane.

*Methyl* l-*α-hydroxy-β-phenylpropionate*, $CH_2Ph\cdot CH(OH)\cdot CO_2Me$, prepared by the esterification of the *l*-hydroxy-acid with methyl alcohol and hydrogen chloride, boils at 155°/17 mm. It became solid on the addition of a nucleus of the ethyl *l*-ester (McKenzie and Barrow, T., 1911, **99**, 1922), and then melted at 47·5—48·5°. It separates from ethyl alcohol in needles, and may also be crystallised conveniently from light petroleum. It is readily soluble in acetone or benzene. Its behaviour resembles that of the ethyl *l*-ester, inasmuch as it is dextrorotatory in ethyl-alcoholic solution:

$$l=2,\ c=3{\cdot}131,\ \alpha_D^{18\cdot5}\ +0{\cdot}40°,\ [\alpha]_D^{18\cdot5}\ +6{\cdot}4°.$$

In acetone solution:

$$l=2,\ c=3{\cdot}879,\ \alpha_D^{19\cdot5}\ -0{\cdot}66°,\ [\alpha]_D^{19\cdot5}\ -8{\cdot}5°.$$

In benzene solution:

$$l=2,\ c=3{\cdot}092,\ \alpha_D^{18}\ -0{\cdot}75°,\ [\alpha]_D^{18}\ -12{\cdot}1°.$$

0·1353 gave 0·33 $CO_2$ and 0·0815 $H_2O$. C=66·5; H=6·7.

$C_{10}H_{12}O_3$ requires C=66·6; H=6·7 per cent.

The methyl *l*-ester (3·4 grams) was added to the Grignard reagent prepared from methyl iodide (30 grams). The yield of pure glycol amounted to 2·5 grams.

l-*βγ-Dihydroxy-α-phenyl*isopentane, $CH_2Ph\cdot CH(OH)\cdot CMe_2\cdot OH$, crystallises in colourless prisms, and melts at 73—74°. It is easily soluble in ether, ethyl alcohol, acetone, or benzene, and may be crystallised conveniently from light petroleum (b. p. 60—80°), in which it is sparingly soluble at the ordinary temperature. Its solution in cold concentrated sulphuric acid is yellowish-brown, and it exhibits a pronounced green fluorescence:

0·134 gave 0·3605 $CO_2$ and 0·1083 $H_2O$. C = 73·4; H = 9·0.

$C_{11}H_{16}O_2$ requires C = 73·3; H = 9·0 per cent.

In acetone solution:

$$l = 2,\ c = 3{\cdot}424,\ \alpha_D^{20}\ -4{\cdot}85^\circ,\ [\alpha]_D^{20}\ -70{\cdot}8^\circ.$$

In benzene solution:

$$l = 2,\ c = 2{\cdot}898,\ \alpha_D^{20}\ -3{\cdot}92^\circ,\ [\alpha]_D^{20}\ -67{\cdot}6^\circ.$$

The triboluminescence exhibited by this glycol was very faint.

### d-*βγ-Dihydroxy-α-phenyl-γ-ethyl*-n-*pentane.*

This glycol was prepared by the interaction of ethyl *d*-α-hydroxy-β-phenylpropionate (3 grams) and the Grignard reagent obtained from ethyl iodide (25 grams). The crude solid (2·7 grams) was purified by three crystallisations from light petroleum.

d-*βγ-Dihydroxy-α-phenyl-γ-ethyl*-n-*pentane*,

$CH_2Ph{\cdot}CH(OH){\cdot}CEt_2{\cdot}OH$,

separates in rectangular needles, and melts at 74—75°. It is readily soluble in cold ethyl alcohol, ether, benzene, or acetone, and sparingly so in cold light petroleum. Its solution in cold concentrated sulphuric acid is yellow and fluorescent:

0·1177 gave 0·3234 $CO_2$ and 0·101 $H_2O$. C = 74·9; H = 9·6.

$C_{13}H_{20}O_2$ requires C = 74·9; H = 9·7 per cent.

In acetone solution:

$$l = 2,\ c = 2{\cdot}54,\ \alpha_D^{18}\ +2{\cdot}98^\circ,\ [\alpha]_D^{18}\ +58{\cdot}7^\circ.$$

In benzene solution:

$$l = 2,\ c = 2{\cdot}734,\ \alpha_D^{18}\ +2{\cdot}49^\circ,\ [\alpha]_D^{18}\ +45{\cdot}5^\circ.$$

The compound was strongly triboluminescent.

### d-*βγ-Dihydroxy-αδ-diphenyl-β-benzyl*-n-*butane.*

The additive compound formed from the interaction of ethyl *d*-α-hydroxy-β-phenylpropionate (2·1 grams) and the Grignard reagent prepared from 23 grams of benzyl chloride was decomposed by ice and sulphuric acid. The glycol is sparingly soluble in ether, and it accordingly separated. It was purified by crystallisation from ethyl alcohol. Yield, 1·8 grams.

d-*βγ-Dihydroxy-αδ-diphenyl-β-benzyl*-n-*butane*,

$CH_2Ph{\cdot}CH(OH){\cdot}C(Ph{\cdot}CH_2)_2{\cdot}OH$,

is sparingly soluble in cold and hot ethyl alcohol, from which it separates in colourless needles, m. p. 182·5—183·5°. It is sparingly soluble in cold ether, benzene, or light petroleum, and moderately so in cold acetone. It is not so soluble in cold sulphuric acid as the other glycols; its solution is orange-coloured:

0·1016 gave 0·3094 $CO_2$ and 0·0665 $H_2O$. C=83·1; H=7·3.

$C_{23}H_{24}O_2$ requires C=83·1; H=7·3 per cent.

In acetone solution:

$$l=4,\ c=0{\cdot}5016,\ \alpha_D^{18}+0{\cdot}15^\circ,\ [\alpha]^{18}+7{\cdot}5^\circ.$$

In benzene solution:

$$l=4,\ c=0{\cdot}3928,\ \alpha_D^{18}-0{\cdot}35^\circ,\ [\alpha]_D^{18}-22{\cdot}3^\circ.$$

The compound exhibited a feeble triboluminescence.

The expenses of this investigation have been mainly met by a grant from the Government Grant Committee of the Royal Society, for which we are glad to take this opportunity of expressing our thanks.

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London, E.C.

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## XVII.—*Dibenzyl- and Diphenyl-silicols and -silicones.*

By Geoffrey Martin.

Kipping (T., 1912, **101**, 2108) states that I (*Ber.*, 1912, **45**, 403) "gave a very erroneous account" of diphenylsilicol, suggests that I was "misled" by false analogies (p. 2112), that "the difficulties presented by the investigation . . . were altogether exceptional, and might have led into error a much more experienced chemist" (p. 2112), and says that he "failed to confirm" my "more important experiments" (p. 2108). The reader, without my paper before him, and with no special knowledge of the subject, would certainly gather that Kipping had arrived at conclusions very different from mine, and that I had made a series of grave mistakes, which he now put right. That such conclusions would be entirely incorrect is shown by a brief contrast between Kipping's and my results:

### *Properties of Diphenylsilicol.*

| Kipping (T., 1912, **101**, 2106—2166). | Martin (*Ber.*, 1912, **45**, 403—409). |
|---|---|
| 1. Two "crystalline modifications" (p. 2112). | 1. Two "*Modifikationen*" composed of different crystals (pp. 405—406). |
| 2. Both forms decompose on heating, evolving water with effervescence (pp. 2112, 2122, 2123, 2136, etc.). | 2. Both forms decompose on heating, evolving water with effervescence (p. 405). |
| 3. Both forms liquefy at the moment of decomposition, forming silicones (pp. 2109, 2136). | 3. Both forms liquefy at the moment of decomposition, forming a glue-like product (p. 406). |
| 4. The form with the higher liquefying point is the more stable (pp. 2112, 2124). | 4. The form with the higher liquefying point appears to be the more stable (p. 406). |

*Properties of Diphenylsilicol* (continued).

| KIPPING (T., 1912, **101**, 2106—2166). | MARTIN (*Ber.*, 1912, **45**, 403—409). |
|---|---|
| 5. The lower liquefying form can pass into the higher form, either spontaneously (pp. 2120, 2124) or on heating (pp. 2112, 2124). | 5. The one form appears capable of passing into the other, and vice versa (p. 406). |
| 6. The temperature of liquefaction or decomposition varies with rate of heating and state of division of the substance (p. 2122). | 6. The temperature of liquefaction (decomposition) varies with the rate of heating (p. 405). |
| 7. The one form liquefies with decomposition below 132°,* the other at about 160° (pp. 2112, 2124). | 7. The one form liquefies with decomposition at about 140°,* the other at about 160° (p. 405). |
| 8. Both forms:<br>soluble in potassium hydroxide solution;<br>readily soluble in ether;<br>sparingly soluble in chloroform;<br>practically insoluble in light petroleum (p. 2122). | 8. Both forms:<br>soluble in potassium hydroxide solution;<br>readily soluble in ether;<br>sparingly soluble in chloroform;<br>only sparingly soluble in light petroleum (p. 405). |
| 9. Pure specimens "usually decompose and liquefy completely below 132°,* although very occasionally the decomposition does not occur until the temperature has been raised to about 160°" (p. 2112). | 9. Die so erhaltene Krystallmasse schmolz bei ungefähr 160° unter Aufschäumen (infolge Abspaltung von Wasser); der Schmelzpunkt schwankte etwas mit der Schnelligkeit des Erhitzens, und in einigen Fällen wurden auch Produkte gewonnen, die sich bereits bei 140° * verflüssigten (p. 405). |

* The difference of about 8° between the decomposition points of my modification and that of Kipping is probably due to the fact that I heated more rapidly, using a larger quantity of material than he did.

Since Kipping's account of diphenylsilicol agrees closely with mine, his remark (*loc. cit.*, p. 2108, footnote) that in my paper I "unfortunately . . . gave a very erroneous account" of diphenylsilicol, is unjustifiable, and all the more so as he has added nothing of importance to the facts already published in my paper (*loc. cit.*).

Turning to Kipping's statement (*loc. cit.*, p. 2108) that he "failed to confirm" some of my "more important experiments," the following tabulation of my results and those obtained by Kipping shows that the "confirmation" is close (compounds marked † are described for the first time):

| KIPPING (*loc. cit.*). | MARTIN (*loc. cit.*). |
|---|---|
| 1. "*Dianhydrotrisdiphenylsilicanediol,*" massive, transparent, rhomboidal crystals, m. p. 111—112° (p. 2131). | 1. † "Grosse, durchsichtige, flache Rhomben," "die so erhaltenen Krystalle schmolzen bei 110° bezw. nach nochmaligem umlösen bei 111°"* (p. 407). |

* Kipping misquotes (p. 2129) my melting point as 100—111°.

| Kipping (*loc. cit.*). | Martin (*loc. cit.*). |
|---|---|
| 2. † "Anhydrobisdiphenylsilicanediol," m. p. 113—114°. | 2. Not isolated in a pure state. |
| 3. Silicone, $(SiPh_2O)_3$, m. p. 188—189° (Dilthey's silicone). | 3. Silicone, $(SiPh_2O)_3$, m. p. 188° (Dilthey's silicone). |
| 4. † Silicone, $(SiPh_2O)_4$, m. p. 200—201°, "crystals, melting fairly sharply at 184—186°" were obtained; "this apparently pure . . . compound . . . by repeated fractional crystallisation . . . was gradually resolved into the pure compound, melting at 200—201° . . ." (p. 2140). | 4. "In sehr kleinen Quantitäten erhielt ich hierbei auch zwei krystallinische Körper vom Schmp. 125° bezw. 186°, die mit dem Diltheyschen Silicon nicht identisch und wahrscheinlich bisher noch nicht beschrieben sind. Ich habe sie jedoch nicht in genügenden Mengen gewinnen können, um ihre Natur festzustellen" (p. 408). |
| 5. Existence not disputed (p. 2126). | 5. † Silicone, $(SiPh_2O)_n$, m. p. over 360°, white, amorphous powder. |
| 6. ,, ,, ,, | 6. † Silicone, $(Si(CH_2Ph)_2O)_n$, m. p. about 200°, white, amorphous powder. |
| 7. *Phenylbenzylsilicol*, $SiPh(CH_2Ph)(OH)_2$, silky needles, soluble in potassium hydroxide, m. p. 106°, when rapidly heated. Resembles dibenzylsilicol, decomposed in solution by hydrochloric acid (p. 2164). | 7. † *Phenylbenzylsilicol*, $SiPh(CH_2Ph)(OH)_2$, white, crystalline substance, m. p. 104°. Resembles dibenzylsilicol, m. p. 101°. When moist, is decomposed by hydrochloric acid fumes (p. 405). |

I now deal with a misrepresentation of my paper. Kipping requested me to look for two "isomerides" of diphenylsilicol, Kipping and Robison (T., 1908, **93**, 441) having just described two "isomerides" of dibenzylsilicol, one melting at 74° and the other at 101°, which were "unaccountable" on the current ideas of stereoisomerism. This was the origin of my paper. However, Kipping and Robison's new "isomerides" were really substances very different from each other in molecular structure and molecular weight; the one "isomeride," m. p. 74°, having the complex structure $HO{\cdot}Si(C_7H_7)_2{\cdot}O{\cdot}Si(C_7H_7)_2{\cdot}OH$, and crystallising with one molecule of water, whilst the other "isomeride," m. p. 101°, is the "real" dibenzylsilicol (T., 1912, **101**, 2143). Kipping, however, now asserts that I have erroneously described two "isomeric" forms of diphenylsilicol; thus he says (P., 1912, **28**, 244):

"The *isomeric* 'diphenylsilicols' described by Martin (*Ber.*, 1912, **45**, 403) as melting at about 140° and 160° respectively, were probably impure specimens of diphenylsilicanediol (diphenylsilicol), and the methods which he gave for the conversion of these supposed isomerides into one another do not bring about any isomeric change."

In the *Transactions* (*loc. cit.*) he amplifies his statements, referring to my "isomerides" on p. 2108 and p. 2110, whilst on p. 2112 he says:

"there does not seem to be any evidence of the existence of the isomeric diphenylsilicanediols (diphenylsilicols) described by Martin, and judging from the methods of preparation and the decomposing points of his supposed isomerides, both must be regarded as impure specimens of the diol (diphenylsilicol). In justice to Martin, however, it should perhaps be pointed out that not only was he misled by a presumed analogy between dibenzylsilicanediol and diphenylsilicanediol, etc."

On p. 2125 he even "explains" how my error arose:

"One further point remains to be considered, namely, how Martin was led to believe that the preparations which he regarded as isomeric diphenylsilicols could be transformed one into the other by the methods which he describes (*loc. cit.*). According to his statements, when the "isomeride" decomposing at about 160° was dissolved in an aqueous solution of potassium hydroxide, and the solution then treated with acids, the "isomeride" decomposing at about 144° was obtained, but if alcoholic potassium hydroxide was used, the original "isomeride" decomposing at about 160° was precipitated. These statements are doubtless incorrect in so far as any question of isomerism is concerned, but . . . the actual observations are to be accounted for as follows, etc."

Now all this is most misleading and inaccurate, because in the whole of my paper in the *Berichte* (*loc. cit.*) not a single mention or reference, direct or indirect, is made of the existence of isomeric diphenylsilicols! Indeed, I actually use the same words as Kipping ("modifications"), and give no speculations of any kind in my paper regarding the molecular structure of my two "modifications"; even the abstract of my paper (A., 1912, **102**, i, 404) refers to two "forms" only.

Kipping also denies (see preceding quotations) that I transformed one modification of diphenylsilicol into the other, and vice versa. Yet he himself quotes several cases of the change of one modification into the other (see *loc. cit.*, pp. 2112, 2120, 2123, 2124), and on p. 2124 states that this is a result which "appears to be fully established," so that it is not apparent why he should doubt my own statements to the same effect. Moreover, his "explanation" (p. 2125) of my "transformations," based on the assumption of the presence of much impurity insoluble in potassium hydroxide, is incorrect for the simple reason that I isolated my two modifications in a pure form, both soluble in potassium hydroxide without giving a residue. In the first place, starting from my product of low melting point, I obtained by careful and laborious crystallisation (which extended over many weeks) a pure specimen of the modification of lower melting point (m. p. 140°), the analysis of which agreed well with the formula $SiPh_2(OH)_2$, and the compound was completely soluble in potassium hydroxide to a perfectly clear solution. Now this substance was simply Kipping's diphenylsilicol of lower melting point (likewise obtained by a process of crystallisation from impure residues! see p. 2120), the difference between the decomposing points (m. p.'s) given by him and myself being simply due to the different rates of heating different quantities of material. In the second case my modification of higher decomposing point (160°) was also obtained pure by week-long continuous recrystallisation of the product of high melting point. Estimations of carbon, hydrogen, and silicon agreed correctly with the formula $SiPh_2(OH)_2$, and the compound dissolved in potassium hydroxide without any residue. Consequently, as both modifications gave correct analyses, were different in crystalline appearance even to the naked eye, differed by at least 20° in their liquefying points, differed also in their solubilities, and were both completely soluble without residue in aqueous potassium hydroxide, I must, until the contrary is distinctly proved, reaffirm that my two modifications of diphenylsilicol do most undoubtedly exist, and that Kipping has merely "rediscovered" them in his newly-described two "crystalline modifications" of diphenylsilicol.

Lastly, I wish to point out that Kipping's "explanation" (p. 2125) of my results is really no explanation at all. The cause of the rise of liquefying point of the diphenylsilicol from 140° (Kipping, 132°) to 160° is, according to Kipping's own view (*loc. cit.*, pp. 2112, 2124), simply due to the change from one crystalline modification (liquefying at 132° or 140°) into another crystalline state (liquefying at 160°). Kipping does not consider that a trace of "impurity" of itself would cause the liquefying points to rise* by at least 20°, but merely acts, in his own words (p. 2124), in "causing the crystalline transformation of the diol to take place." Hence, even if my impure substance did contain a small trace of "impurity," it would, so long as it melted at 160°, according to Kipping's own explanation, still be in the one crystalline state, whilst when its melting point fell to 140° (132° Kipping) this would likewise be solely due to it passing into the other crystalline state. So that, on Kipping's own "explanation," I must have had the two crystalline modifications in my hands!

Kipping finally concludes (p. 2123):

"It seems necessary to conclude that diphenylsilicanediol (diphenylsilicol) is dimorphous; that the crystalline form which . . . decomposes below 132° may pass into a more stable one, which does not decompose until about 160°."

There seems little difference between this and my earlier conclusion (*loc. cit.*) that two modifications of diphenylsilicol exist, one with the liquefying point 160°, described as "gegenüber hohen Temperaturen etwas widerstandfähiger war, als die andere" (Martin, *loc. cit.*, p. 406), and the other with a lower liquefying point of about 140° (the exact temperature depending on rate of heating and amount of material heated), and that one form could pass into the other, and vice versa.

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* A trace of impurity would rather tend to depress the liquefying point.

## XVIII.—*The Photography of Absorption Spectra.*

By Thomas Ralph Merton, B.Sc.(Oxon.).

Almost all the work on absorption spectra in recent years has been carried out by Hartley and Huntington's method, which consists in photographing a series of spectra of a light source on the same plate through increasing thicknesses of the absorbing substance. By measuring the wave-lengths at which "absorption begins" with the varying thicknesses of solution, a curve may be drawn which represents to some extent the nature of the absorption. The results obtained by this method are only of a very qualitative nature, and Houstoun and his colleagues in a series of papers (*Proc. Roy. Soc. Edin.*, 1911, **31**, 521) have obtained accurate curves of the extinction-coefficients of a number of solutions by the use of a spectrophotometer. A similar method has been used by the author in an investigation of the absorption of uranous chloride solutions (*Proc. Roy. Soc.*, 1912, *A*, **87**, 138).

Whilst measurements with the spectrophotometer can be made to give accurate quantitative results, it must be admitted that a considerable amount of practice is required before concordant readings can be obtained, and the probable error of the observations varies with the wave-length of the light used. It seems, therefore, desirable to find some means of obtaining quantitative results by a simple photographic method.

The objections to the older photographic method may be summarised as follows:

(i) The point where "absorption begins," which is used in plotting the curves, is always somewhat indefinite.

(ii) The sensitiveness of the photographic plate varies with light of different wave-length. This not only introduces errors in the shape of the curve, but may in certain circumstances give a wrong reading of the maximum.

(iii) There is no linear relationship between the density of the image on the photographic plate and the intensity of the light which produces it.

(iv) The density of the image is not proportional to the product of the intensity of the light by the time of exposure, that is to say, doubling the time of exposure and halving the intensity of the light will not produce the same effect on the photographic plate.

It is evident, therefore, that on account of the anomalous behaviour of the photographic plate, any method which is to give accurate results must be a null method. It must comply with the principle laid down by Houstoun (*loc. cit.*), that two sources of light can only be considered of equal intensity when, in the same time, they produce images of equal density on adjacent portions of the same photographic plate.

A number of experiments were made by the following method, which is similar in principle to that used by Houstoun in his investigations in the ultra-violet.

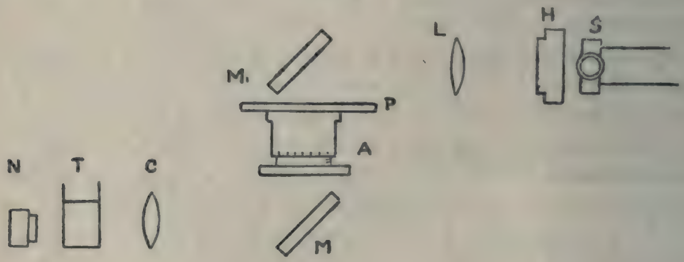
The light from a straight filament Nernst lamp, after passing through a rectangular glass tank to remove heat rays, was made approximately parallel by a collimating lens. It then passed through two nicol prisms and a glass cell to the slit of the spectrograph. The rotation of one of the nicols could be read on a divided circle. It was thus possible to set the nicols to any desired extinction. The spectrograph used was a large Hilger wave-length spectroscope with a 21-inch focus spectrograph attachment in place of the telescope. It was provided with a wave-length scale, which could be photographed on the plate adjacent to the spectra. The method consists in taking a number of spectra on the same plate in the following manner. Suppose the thirteen exposures were made on the plate. The cell was filled with the solution to be examined, and the angle between the nicols was set to zero. With this arrangement strips 1, 4, 7, 10, and 13 were exposed, the time of exposure being accurately controlled by a stop-watch and a photographic shutter. The cell was now replaced by an exactly similar cell filled with the solvent, and strips 2, 3, 5, 6, 8, 9, 11, and 12 were exposed through a series of different densities which were obtained by rotating one of the nicols. We thus have on the plate five absorption spectra, with a photograph taken through a known density adjacent to each. It is therefore only necessary to pick out the wave-lengths on each strip at which the density is the same as that of the adjacent standard strip.

This gives the necessary data for plotting a quantitative extinction curve.

There is, however, an objection to this method, namely, that there is one particular density of the photographic plate at which the points of equal density on adjacent strips can be accurately found. This is due partly to the form of the curve connecting the intensity of the light with the density which it produces on the plate, but chiefly to the fact that the points of equal density in either very faint or very dense regions are hard to detect. This might be overcome by varying the exposure on the different sets of strips (taking care that each strip has had the same exposure as those with which it is to be compared). Practically, however, this involves very short exposures, which are liable to be inaccurate, for low extinctions, and very long exposures, which makes the method laborious, at high extinctions. A method has been devised, which, it is believed, overcomes these difficulties and provides a simple and accurate method of obtaining extinction curves.

After examining a number of the so-called neutral-tinted glass plates, it was found that the neutral screens supplied by Messrs. Sanger-Shepherd (which are made of an emulsion between two glass plates) have an extinction-coefficient which is practically constant throughout the visible spectrum. This was verified by means of a Houstoun spectrophotometer.

FIG. 1.



The method finally adopted was to photograph a series of strips through a neutral plate of carefully standardised extinction, and to photograph between these the spectrum through different thicknesses of the absorbing substance. By choosing a suitable time of exposure the points of equal extinction can be made to occur in each pair of strips at the density best suited for comparison.

A diagram of the apparatus used is shown in Fig. 1. The light from the Nernst lamp *N*, after passing through the water tank *T* and the collimating lens *C*, is twice reflected by the mirrors *MM*, and is concentrated on the slit *S* by the lens *L* after passing through the photographic shutter *H*. A Zeiss variable absorption cell *A* was placed between the mirrors *MM*. The thickness of the absorbing layer in this cell can be accurately measured by means of a screw

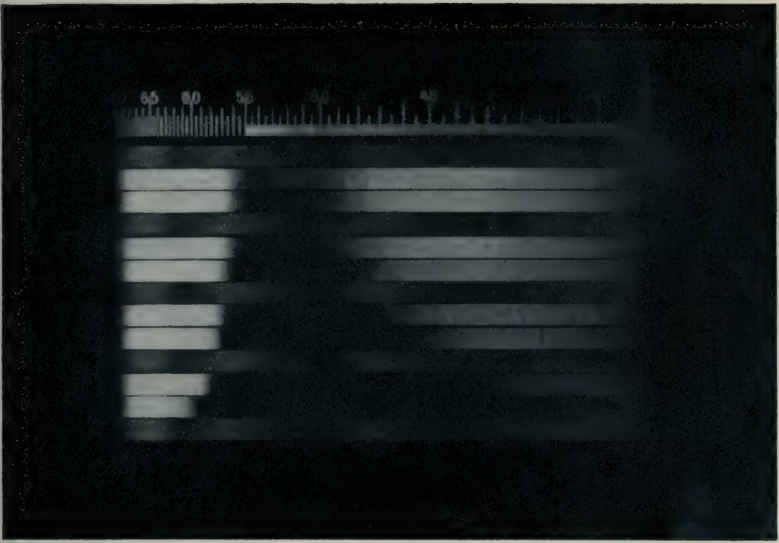
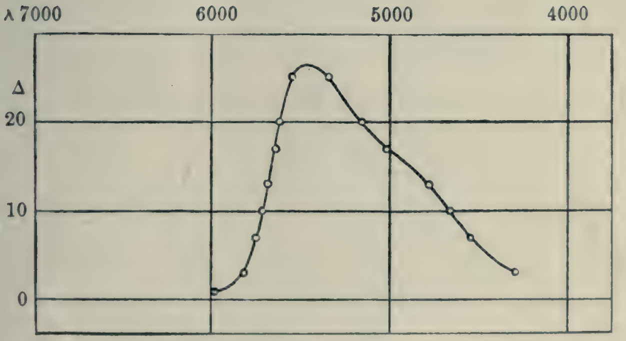


FIG. 2.



[*To face p.* 126.

adjustment, and the instrument has been found to be admirably suited to the work.

In conducting the experiment, the cell *A* was filled with the pure solvent, and the standardised plate *P* was laid on it. ($\Delta = 1$ has been found to be a suitable density for the standard plate.) Strips 1, 4, 7, 10, and 13 were exposed. The plate was removed, and the cell filled with the solution to be investigated. Strips 2, 3, 5, 6, 8, 9, 11, and 12 were now exposed through various thicknesses of solution. As a typical example is given the plate taken of an aqueous solution of magenta, together with the extinction curve (Fig. 2) drawn from it.

In conclusion, it may be said that the method offers very little practical difficulty; the time taken in the measurement is little longer than with the method of Hartley, and quantitative results can be obtained without involving the use of costly apparatus.

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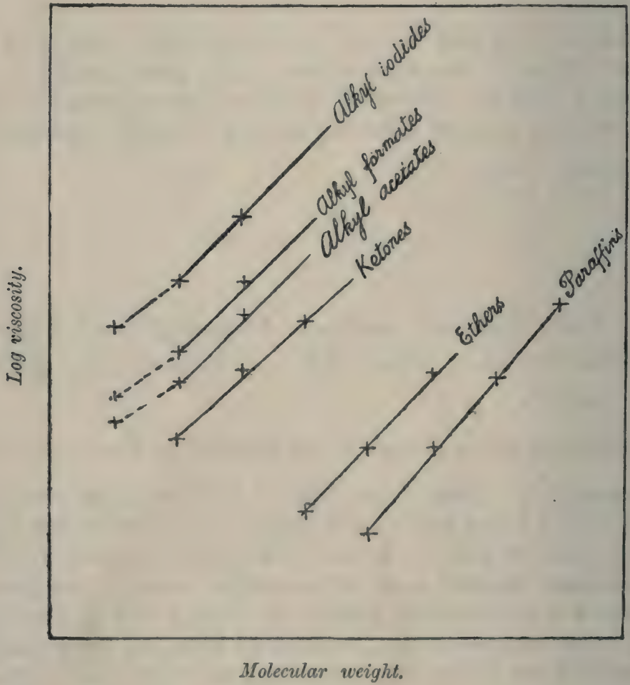
# XIX.—*The Relation between Viscosity and Chemical Constitution. Part VI. Viscosity an Additive Function.*

By ALBERT ERNEST DUNSTAN AND FERDINAND BERNARD THOLE.

SOME time ago (*J. Chim. Phys.*, 1909, **7**, 210) we drew attention to the fact that a linear relationship exists between molecular weights and logarithms of viscosity in several homologous series. Having in the meantime amassed more experimental material, we desire in the present communication further to develop this generalisation. Owing to the kindness of Dr. Pickard, we have had the opportunity of examining two of the long homologous series prepared by himself and Mr. Kenyon (T., 1911, **99**, 45). In one of these series, the methylalkylcarbinols, all the eight members examined, ranging from *iso*propyl alcohol to methylnonylcarbinol, give log viscosities which lie on a straight line. In the other series, the *iso*propylalkylcarbinols, the agreement is scarcely so good, but a glance at the figure will show that a straight line adequately represents the relationship between molecular weight and log viscosity. Further, in collaboration with Dr. Hilditch (see Part VII. of this series), we have examined a long series of dibasic esters from the oxalic to the sebacic term. Little regularity is met with in this case until the first three members are passed, since conjugation effects are pronounced in these cases, but from glutaric ester onwards the linearity of the curve becomes marked. Gartenmeister (*Zeitsch. physikal. Chem.*, 1890, **6**, 524) measured the viscosities of the first nine members of the fatty acids at 20°, and we find that on plotting log viscosity against molecular weights a linear curve is afforded from the third member onwards. Adding to these cases, all of which embody an homologous series of some length, the measurements of Thorpe and Rodger (*Phil. Trans.*, 1894, *A.*, **185**, 397)

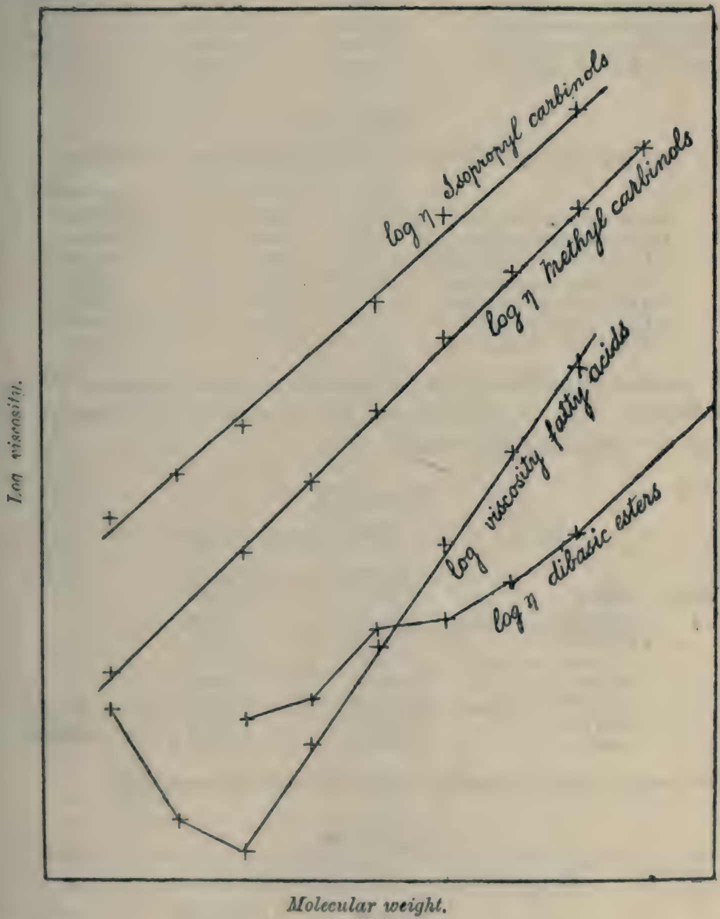
FIG. 1.



for the first four or five members of some ten homologous series, we find the same linear relationship, and we suggest that additive values of log viscosity for the more important radicles may well be deduced.

It should be mentioned at the outset that hydroxylated compounds, which almost invariably give abnormally high values for viscosity, are not suitable for such a purpose; this point is apparent when the slope of the curves is considered, for whereas in Fig. 1 the log-viscosity–molecular-weight curves for such groups as paraffins, ethers, esters, and ketones are parallel, it will be seen in Fig. 2 that the curve for the acids is by no means parallel with that for the carbinols. Further, as with almost every physical property, the results for the first one or two members of an homologous series tend to anomaly, and these should not be included.

FIG. 2.



Whilst employing our own determinations to support the thesis that log viscosity is an additive function, we have used chiefly the data of Thorpe and Rodger at 20° as a basis for the calculated values.

We have taken logarithms of viscosity × $10^5$ to avoid barred characteristics.

## TABLE I.

*Methylalkylcarbinols at* 25° (Pickard and Kenyon).

| | Viscosity. | $\log \eta \times 10^5$. | $\Delta CH_2$. |
|---|---|---|---|
| *iso*Propyl alcohol | 0·0206 | 3·3139 | |
| Methyl-*n*-propylcarbinol | 0·0309 | 3·4901 | 0·0881 |
| Methyl-*n*-butylcarbinol | 0·0398 | 3·6001 | 0·1100 |
| Methyl-*n*-amylcarbinol | 0·0506 | 3·7037 | 0·1036 |
| Methyl-*n*-hexylcarbinol | 0·0655 | 3·8162 | 0·1125 |
| Methyl-*n*-heptylcarbinol | 0·0828 | 3·9180 | 0·1018 |
| Methyl-*n*-octylcarbinol | 0·1010 | 4·0043 | 0·0863 |
| Methyl-*n*-nonylcarbinol | 0·1228 | 4·0892 | 0·0849 |

## TABLE II.

iso*Propylalkylcarbinols at* 25° (Pickard and Kenyon).

| | Viscosity. | $\log \eta \times 10^5$. |
|---|---|---|
| Methyl*iso*propylcarbinol | 0·0351 | 3·5449 |
| Ethyl*iso*propylcarbinol | 0·0403 | 3·6050 |
| *n*-Propyl*iso*propylcarbinol | 0·0474 | 3·6761 |
| *n*-Butyl*iso*propylcarbinol | 0·0709 | 3·8505 |
| *n*-Amyl*iso*propylcarbinol | 0·0729 | 3·8629 |
| *n*-Hexyl*iso*propylcarbinol | 0·1018 | 4·0077 |
| *n*-Octyl*iso*propylcarbinol | 0·1431 | 4·1557 |

A marked abnormality in the fourth member (compare Pickard and Kenyon, *loc. cit.*) throws out the regularity of this series as a means of obtaining $CH_2$ values.

## TABLE III.

*Esters of the Oxalic Series at* 25°.

| | Viscosity. | $\log \eta \times 10^5$. | $\Delta CH_2$. |
|---|---|---|---|
| Diethyl oxalate | 0·01751 | 3·2433 | |
| ,, malonate | 0·01875 | 3·2730 | |
| ,, succinate | 0·02400 | 3·3802 | |
| ,, glutarate | 0·02480 | 3·3945 | |
| ,, adipate | 0·02768 | 3·4425 | |
| ,, pimelate | 0·03280 | 3·5160 | |
| ,, suberate | 0·04036 | 3·6059 | 0·0899 |
| ,, sebacate | 0·05073 | 3·7053 | 0·0994 |

This series shows anomaly up to the glutaric member.

## TABLE IV.

*Fatty Acids at* 20° (Gartenmeister).

| | Viscosity. | $\log \eta \times 10^5$. | $\Delta CH_2$. |
|---|---|---|---|
| Formic acid | 0·01804 | 3·2562 | |
| Acetic ,, | 0·01232 | 3·0906 | |
| Propionic ,, | 0·01107 | 3·0441 | |
| Butyric ,, | 0·01598 | 3·2036 | 0·1595 |
| Valeric ,, | 0·02236 | 3·3495 | 0·1459 |
| Hexoic ,, | 0·03201 | 3·5053 | 0·1558 |
| Heptoic ,, | 0·04356 | 3·6391 | 0·1338 |
| Octoic ,, | 0·05749 | 3·7596 | 0·1205 |
| Nonoic ,, | 0·08319 | 3·9201 | 0·1605 |

### *The Value for* $CH_2$.

| Substance. | $\eta$. | $\Delta \log \eta \times 10^5$ for $CH_2$. | |
|---|---|---|---|
| Hexane | 0·00320 | 0·109 | 0·109 paraffins |
| Heptane | 0·00411 | 0·117 | |
| Octane | 0·00538 | | |
| *iso*Hexane | 0·00300 | 0·102 | |
| *iso*Heptane | 0·00379 | | |
| Ethyl iodide | 0·00583 | 0·102 | 0·102 alkyl iodides |
| Propyl ,, | 0·00737 | | |
| *iso*Propyl iodide | 0·00690 | 0·101 | |
| *iso*Butyl ,, | 0·00870 | | |
| Methyl propyl ether | 0·002515 | 0·101 | 0·108 ethers |
| Ethyl ,, ,, | 0·003175 | | |
| Propyl ,, | 0·00420 | 0·126 | |
| Ethyl ,, | 0·002345 | | |
| Propyl ,, | 0·00420 | 0·111 | |
| Methyl propyl ,, | 0·002515 | | |
| ,, *iso*butyl ,, | 0·003065 | 0·092 | |
| Ethyl ,, ,, | 0·003785 | | |
| Ethyl acetate | 0·00449 | 0·112 | 0·107 esters |
| Propyl ,, | 0·00581 | | |
| Methyl propionate | 0·00454 | 0·103 | |
| ,, butyrate | 0·00575 | | |
| Acetone | 0·003225 | 0·096 | 0·106 ketones |
| Methyl propyl ketone | 0·00501 | | |
| ,, ethyl ,, | 0·00423 | 0·117 | |
| Acetone | 0·00501 | | |
| Propyl alcohol | 0·0226 | 0·116 | 0·116 alcohols |
| Butyl ,, | 0·0295 | | |
| *iso*Butyl ,, | 0·0391 | 0·115 | |
| *iso*Amyl ,, | 0·0509 | | |
| Methyl sulphide | 0·00293 | 0·091 | 0·091 sulphides |
| Ethyl ,, | 0·00455 | | |

Mean value for 16 pairs = **0·107.**

### *Value at 20° of* $\log \eta \times 10^5$ *for the Chief Groups.*

$CH_2$ ................. 0·107

*Hydrogen.*—Subtracting the $CH_2$ value from log viscosity × $10^5$ of the paraffins, we get:

| | | |
|---|---|---|
| From hexane | 0·931 | Mean for H = 0·934 |
| ,, heptane | 0·932 | |
| ,, octane | 0·938 | |

*Alcoholic Hydroxyl.*—Subtracting the value for $CH_2$ and H from the log viscosity × $10^5$ of the higher alcohols, we get:

| | | |
|---|---|---|
| From propyl alcohol | 2·097 | Mean for OH = 2·102 |
| ,, butyl ,, | 2·108 | |

*Ethereal Oxygen.*—Subtracting the value for the alkyl radicles from the log viscosity × $10^5$ of the ethers, we get:

| | | |
|---|---|---|
| From methyl propyl ether | 0·105 | Mean for O = 0·098 |
| ,, ethyl ,, ,, | 0·099 | |
| ,, propyl ether | 0·113 | |
| , ethyl ,, | 0·074 | |

*Carbethoxyl.*—Subtracting the value for the alkyl radicles from log viscosity × $10^5$ of the higher fatty esters, we get:

| | | |
|---|---|---|
| From ethyl propionate ............... | 1·583 | Mean for $CO_2Et = 1·573$ |
| ,, ,, butyrate.................. | 1·570 | |
| ,, ,, valerate .................. | 1·566 | |

*Carbon.*—Subtracting the value for hydrogen from that of $CH_2$, we get $C = -1·761$.

*Carbonyl* (Ketonic).—Subtracting the value of the alkyl radicles from the log viscosity × $10^5$ of the ketone, we get:

| | | |
|---|---|---|
| From acetone.......................... | 0·427 | Mean for $CO = 0·407$ |
| ,, methyl ethyl ketone ......... | 0·437 | |
| ,, ,, propyl ,, ... ..... | 0·404 | |
| ,, diethyl ketone ............... | 0·372 | |

iso*Union.*—Subtracting the value for the normal compounds from those of the *iso*-isomeride, we get:

| | | |
|---|---|---|
| From *iso*hexane – hexane ..................... | – 0·028 | Mean for *iso*-union = – 0·030 |
| ,, *iso*heptane – heptane ..................... | – 0·035 | |
| ,, *iso*propyl bromide – propyl bromide... | – 0·030 | |
| ,, *iso*propyl iodide – propyl iodide ...... | – 0·029 | |

*Double Bond.*—Subtracting the value for the saturated compound from those of the unsaturated body and two H values, we get:

| | | |
|---|---|---|
| From allyl iodide + 2H – propyl iodide ......... | 1·862 | Mean for double bond 1·847 |
| ,, ,, bromide + 2H – propyl bromide ... | 1·850 | |
| ,, ,, chloride + 2H – propyl chloride ... | 1·840 | |
| ,, ½[diallyl + 4H – hexane] .................. | 1·835 | |

### *Collected Values at 20°.*

| | | | |
|---|---|---|---|
| $CH_2$ ..................... | 0·107 | O (ethereal) ........... | 0·098 |
| H ....................... | 0·934 | $CO_2Et$ ........... ...... | 1·573 |
| OH (alc.) ... ........... | 2·102 | C ....................... | – 1·761 |
| CO (ketonic) ......... | 0·407 | *iso*-union ........... ... | – 0·030 |
| Double bond ......... | 1·847 | | |

The following examples of the synthesis of a molecular value may be given:

(1) *Ethyl Diethylacetoacetate.* $\eta_{20°} = 0·0344$ (Gartenmeister).

$CH_3{\cdot}CO{\cdot}CEt_2{\cdot}CO_2Et$:

$$\begin{array}{lcl} 6CH_2 & = & 0·642 \\ H & = & 0·934 \\ CO & = & 0·407 \\ CO_2Et & = & 1·573 \\ \hline & & 3·556 = \text{log of } 0·0360 \times 10^5 \end{array}$$

(2) iso*Butyl Ethyl Ether.* $\eta_{20^\circ}$ = 0·0376 (Thorpe and Rodger).

$(CH_3)_2CH{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$:
$6CH_2$ = 0·642
O = 0·098
2H = 1·868
2·608
*iso* = −0·030
2·578 = log of **0·0378** × $10^5$

(3) iso*Amylene.* $\eta_{20^\circ}$ = 0·00212 (Thorpe and Rodger).

$(CH_3)_2CH{\cdot}CH{:}CH_2$:
$5CH_2$ = 0·535
: = 1·847
2·382
*iso* = −0·030
2·352 = log of **0·00225** × $10^5$

(4) *Ethyl Acetoacetate.* $\eta_{20^\circ}$ = 0·0168 (Gartenmeister).

$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ ketonic:
$2CH_2$ = 0·214
H = 0·934
CO = 0·407
$CO_2Et$ = 1·573
3·128 = log of **0·0134** × $10^5$

$CH_3{\cdot}C(OH){:}CH{\cdot}CO_2Et$ enolic:
$2CH_2$ = 0·214
OH = 2·102
$CO_2Et$ = 1·573
: = 1·847
5·736
C = − 1·761
3·975 = log of **0·0944**

Therefore, percentage of enolic form = 4·2.

Knorr (*Ber.*, 1911, **31**, 1138, 2767) finds 2 per cent. of enol, and Meyer (*Annalen*, 1911, **380**, 212) obtained 7·5 per cent of enol, a value confirmed by Hantzsch (*Ber.*, 1910, **30**, 49).

In this preliminary communication it must be pointed out that the amount of available data is not sufficient to admit of very satisfactory values being deduced. We hope to examine in the near future a large number of homologous series at a variety of temperatures, so as to amass enough experimental material to render possible the compilation of trustworthy constants.

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## XX.—*The Relation between Viscosity and Chemical Constitution. Part VII. The Effect of the Relative Position of Two Unsaturated Groups on Viscosity.*

By Albert Ernest Dunstan, Thomas Percy Hilditch, and Ferdinand Bernard Thole.

During our examination of the influence of various constitutive features on the viscosity of organic compounds, the results of which (*Zeitsch. Elektrochem.*, 1911, **17**, 929; 1912, **18**, 185) have so far served to correlate that essentially constitutive property with other physical characteristics already studied by previous workers, we have felt that, more particularly as regards the anomalous effects of "unsaturation," the numerous investigations of the past few decades have given but little insight into the underlying causes. It appeared to us that a more detailed study of the mutual influence of two unsaturated groups which are not chemically united in the molecule, but which exert definite effects, either chemical or physical, apparently owing merely to their spatial proximity, might possibly lead further in the desired direction.

We have therefore extended our work on the general correlation of viscosity with other physical properties by examining the viscosities of the members of a number of homologous series of compounds containing two unsaturated groups at varying degrees of proximity to each other.

Instances of effects due to "spatial conjugation," as it has been termed, have not hitherto been met with at all frequently in physico-organic chemistry, although many cases of intramolecular chemical change supposedly due to the nearness in space of the reacting groups will be recalled. Refractivity, one of the most thoroughly studied properties, seems to be insufficiently constitutive to respond to any spatial influences (these, it may at once be said, are in general of a much smaller order than those due to ordinary conjugation), and although optical activity is affected by them (Hilditch, T., 1909, **95**, 1578; *Zeitsch. physikal. Chem.*, 1911, **77**, 482), too little is yet known of the general rules which govern the relation between conjugated unsaturation and molecular rotatory power to permit of any extension of these to the present case. Clarke has, however, shown that spatial proximity and reactivity of unsaturated atoms are connected (T., 1911, **99**, 1927; 1912, **101**, 1788).

As regards the changes in viscosity due to varying constitution, it may be said in general that viscosity is lowered by molecular symmetry, but enhanced by single (and still more by conjugated) unsaturation, by symmetrical conjugation, and by molecular association.

The following illustrations may be given of these general rules:

*Molecular Symmetry.*—The figures for some isomeric primary, secondary, and tertiary amines (Mussell, Thole, and Dunstan, T., 1912, **101**, 1008) show the rapid diminution of viscosity with increasing symmetry of the molecule:

| | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$ |
|---|---|
| $n$-Butylamine | 70·8 |
| Diethylamine | 36·2 |
| (Triethylamine | 26·1) |

The general result that substitution of a hydrogen atom by an alkyl group lowers the molecular viscosity is also due probably to the increased symmetry of the alkylated compound.

*Simple unsaturation*, on the other hand, induces a distinct increase in the value of the expression $\frac{\eta \times 10^6}{\text{Mol. vol.}}$, as is typified by such data as the following:

| | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$. |
|---|---|
| Ethyl *n*-propyl ether | 29·4 |
| Ethyl propargyl ether | 52·2 |

The effect of *conjugated unsaturation* is much more marked; thus we quote:

| | |
|---|---|
| Acetone | 66·9 |
| Mesityl oxide | 84·0 |
| Phorone | 90·6 |
| Safrole | 155·1 |
| *iso*Safrole (conjugated) | 274·2 |

These figures also illustrate the fact that in cases where the conjugated systems form a symmetrical grouping the effect due to any simple molecular symmetry is not only masked, but of itself the *symmetrical conjugation* produces an effect greater than that due to ordinary conjugation (compare mesityl oxide and phorone).

Attention must also be drawn to the fact that the presence of groups which promote molecular association causes an enormously magnified exaltation of molecular viscosity; for example, eugenole, safrole, *iso*eugenole, and *iso*safrole are corresponding allyl and propenyl derivatives of catechol ethers, the only difference being that the eugenoles contain a methyl and an hydroxyl group, the safroles a methylenedioxy-radicle; nevertheless, the hydroxyl group causes a most enormous increase in molecular viscosity:

| | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$. |
|---|---|
| Eugenole | 448·5 |
| *iso*Eugenole | 1759·0 |

Finally, it is interesting to note the enhancing influence of a symmetrical arrangement of unsaturated radicles around a central atom:

| | |
|---|---|
| Aniline | 55·1 |
| Diphenylamine | 61·1 |
| Triphenylamine | 262·0 |
| Benzylamine | 37·0 |
| Dibenzylamine | 39·5 |
| Tribenzylamine | 69·9 |

Bearing in mind, then, these various well-defined constitutive influences, we proceed to the results of our present work on some simple cases of spatial conjugation of unsaturated groups. All the series enumerated in this communication may be represented by the general formula $R\cdot[CH_2]_n\cdot R'$, R and R′ being either the same or different unsaturated radicles, so that the compounds studied were disubstituted normal paraffins.

## Experimental.

Our methods and apparatus remained the same as those described in earlier papers; the experimental material was in some instances purchased from Schuchardt or Kahlbaum, and repurified by distillation or crystallisation, but in the majority of cases we prepared the necessary compounds by methods which, being adapted from current literature, need not be further detailed. Unfortunately, a few of the more interesting substances proved so exceedingly difficult to prepare in the necessary quantities that we had perforce to omit them; this was notably the case with the αδ-dihalogen derivatives of butane. In some other series it was found impracticable to proceed beyond the fourth or fifth member, but the result of an extended series of esters of the normal dicarboxylic acids would appear to indicate that it is only in the lower members that the anomalies which are the primary object of our research present themselves to any marked extent.

### *Series containing Two Identical Unsaturated Radicles.*

### Table I.

*Diethyl Esters of Normal Aliphatic Dicarboxylic Acids at* 25°.

We have measured the viscosities of the members of this series from diethyl oxalate to diethyl sebacate, and our mean results are as follows:

| | $D^{25^\circ}_{4^\circ}$. | $\eta^{25^\circ}$. | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$. |
|---|---|---|---|
| Diethyl oxalate ......... | 1·0725 | 0·01751 | 128·5 |
| ,, malonate ...... | 1·0501 | 0·01875 | 123·2 |
| ,, succinate ...... | 1·0362 | 0·02399 | 142·9 |
| ,, glutarate ...... | 1·0185 | 0·02479 | 132·0 |
| ,, adipate ......... | 1·0110 | 0·02768 | 137·9 |
| ,, pimelate ......... | 0·9929 | 0·03279 | 150·7 |
| ,, suberate ......... | 0·9951 | 0·04036 | 172·6 |
| ,, sebacate ......... | 0·9612 | 0·05073 | 188·6 |

It is evident from the appended curve (Fig. 1) that the viscosities lie on a smooth curve, with the exception of the oxalic and succinic derivatives. The enhanced value for the first member was to be anticipated from our former work on the influence of ordinary conjugation on viscosity; the anomalous figure for the succinic ester must be ascribed to the effect of spatial conjugation, and as appears from the remaining series of this type reported on, this is a general feature of the viscosities of the compounds of the general type $R \cdot CH_2 \cdot CH_2 \cdot R$. It is almost unnecessary to point out that it is this type of substance in which the chemical effects of spatial conjugation (such as elimination of water to form anhydrides, etc.) are most prominent.

The optical activity of the dimenthyl esters of the same series of acids has been shown by one of us (*loc. cit.*) to exhibit similar anomalies due to spatial effects, but, curiously enough, in the latter case the enhanced value does not appear until the adipic ester, in which the carboxylic groups as a whole, rather than their hydroxylic (or alkylic) components, may be supposed from the usual steric hypotheses to be nearest to one another in space.

FIG. 1.

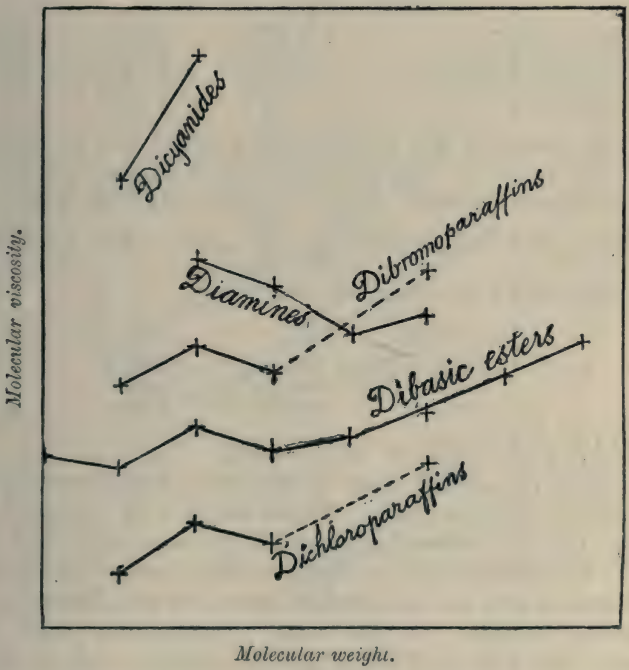


TABLE II.

*Alkylene Dichlorides at* 25°.

| | $D^{25°}_{4°}$. | $\eta^{25°}$. | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$. |
|---|---|---|---|
| Methylene dichloride ................ | 1·3055 | 0·004413 | 67·7 |
| Ethylene dichloride ................ | 1·2525 | 0·007495 | 94·5 |
| Trimethylene dichloride ......... | 1·1770 | 0·008697 | 90·6 |
| Pentamethylene dichloride ...... | 1·0940 | 0·015947 | 123·8 |

### TABLE III.

*Alkylene Dibromides at 25°.*

| | $D_{4^\circ}^{25^\circ}$. | $\eta^{25^\circ}$. | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$. |
|---|---|---|---|
| Methylene dibromide............... | 2·4080 | 0·01225 | 165·0 |
| Ethylene dibromide ............... | 2·1620 | 0·01605 | 184·5 |
| Trimethylene dibromide ......... | 1·9380 | 0·01790 | 171·7 |
| Pentamethylene dibromide ...... | 1·6940 | 0·03040 | 224·0 |

### TABLE IV.

*Alkylene Diamines at 25°.*

| | | | |
|---|---|---|---|
| Ethylenediamine .................. | 0·898 | 0·0154 | 230·0 |
| Trimethylenediamine.............. | 0·884 | 0·0180 | 216·0 |
| Tetramethylenediamine............ | 0·877 | 0·01915 | 191·0 |
| Pentamethylenediamine ......... | 0·873 | 0·02350 | 201·0 |

We also compared the viscosities of malono- and succino-nitriles at 60°; the value for the former is derived by extrapolation from Walden's figures (*Zeitsch. physikal. Chem.*, 1912, **79**, 717), whence $D_{4^\circ}^{60^\circ}$ 1·024, $\eta^{20^\circ}$ 0·0175, so that $\frac{\eta \times 10^6}{\text{Mol. vol.}} = 271$. Our measurements of the viscosity of succinonitrile were:

| Temperature. | $D_{4^\circ}^{t^\circ}$. | $\eta^{t^\circ}$. |
|---|---|---|
| 58·7° | 0·989 | 0·0276 |
| 69·4 | 0·9805 | 0·0236 |
| 83·0 | 0·9765 | 0·0181 |

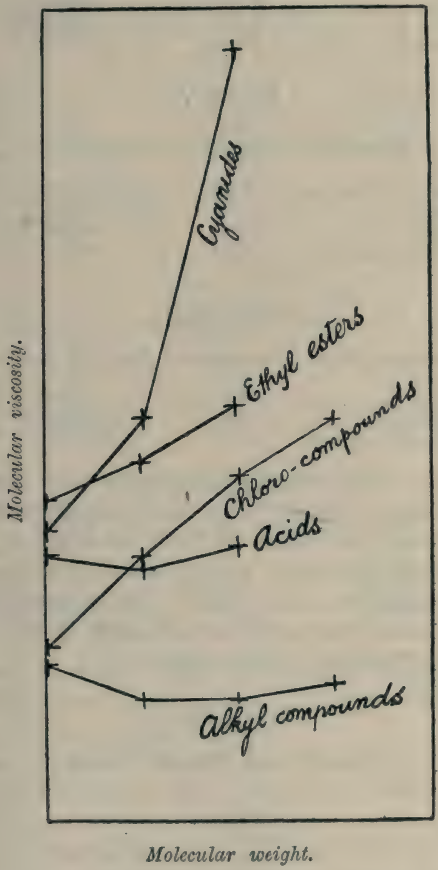
from which $\eta \times 10^6/\text{Mol.vol.}$ at 60° is 336.

The values throughout these further series are accordingly of the same nature as those of the dibasic esters. Of course, in these instances the first terms of each series (corresponding with diethyl oxalate) are compulsorily omitted, namely, the elements chlorine and bromine, and the compounds cyanogen and hydrazine. We commence, therefore, at the terms corresponding with diethyl malonate, and find that the molecular viscosity rises in the next member, the ethylene compound corresponding with diethyl succinate, then falls in the cases of the trimethylene derivatives, and finally, so far as can be judged from the values for the tetra- and penta-methylene compounds, appears to rise steadily with ascending molecular weight in precisely analogous fashion to those of the remainder of the dibasic esters.

The curve for the diamines accentuates the anomaly noticeable in the preceding series, a fact which, in common with certain other results which follow, emphasises the unusually great influence which the amino-complex, like the hydroxyl radicle, exerts on viscosity.

There remains established the existence of similar anomalies in each of these series of compounds, anomalies, moreover, which occur at that term of the homologous series at which accepted steric considerations show the unsaturated groups to be in unusually close spatial proximity.

FIG. 2.



*Series in which the Two Unsaturated Groups are Different* ($R=C_6H_5$; $R'=Cl$, $CO_2H$, $CO_2Et$, $NH_2$, CN, or OH).

For the sake of comparison we have added here the viscosities of some of the phenyl paraffins of analogous structure to their unsaturated substituents, which we deal with subsequently.

### Table V.

*Alkylbenzenes at* 25°.

| | $D_{4°}^{25°}$. | $\eta^{25°}$. | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$. |
|---|---|---|---|
| Benzene ..................... | 0·873 | 0·00601 | 67·3 |
| Toluene......................... | 0·860 | 0·00548 | 51·2 |
| Ethylbenzene ......... ..... | 0·862 | 0·00630 | 51·2 |
| *n*-Propylbenzene ............ | 0·859 | 0·00790 | 56·6 |

### Table VI.

*Monochloroalkylbenzenes at* 25°.

| | | | |
|---|---|---|---|
| Chlorobenzene............... | 1·103 | 0·00758 | 74·3 |
| Benzyl chloride ............ | 1·100 | 0·0128 | 111·5 |
| β-Chloroethylbenzene...... | 1·069 | 0·0191 | 145·0 |
| γ-Chloro-*n*-propylbenzene | 1·056 | 0·0246 | 168·0 |

### Table VII.

*Ethyl Esters of the Homologous Benzoic Acids at* 25°.

| | | | |
|---|---|---|---|
| Ethyl benzoate ............ | 1·041 | 0·01956 | 136·0 |
| Ethyl phenylacetate ...... | 1·029 | 0·02386 | 150·0 |
| Ethyl β-phenylpropionate | 1·014 | 0·03060 | 175·0 |

The viscosities of the corresponding acids were also measured at 130°, and at a degree higher than their respective melting points. The data show that the values at 130°, as would be expected, are much smaller than the values which would be obtained if it were possible to supercool the acids to 25°. Unfortunately, owing to the large and non-linear temperature-coefficient, it was impossible to attempt any extrapolation of the data to 25°.

### Table VIII.

*Homologous Benzoic Acids.*

| | Temp. | $D_{4°}^{t°}$. | $\eta^{t°}$. | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$. |
|---|---|---|---|---|
| Benzoic acid .................. | 130·0° | 1·078 | 0·0126 | 112 |
| | 122·5 | 1·080 | 0·0167 | 146 |
| Phenylacetic acid ........... | 130·0 | 1·043 | 0·0140 | 107 |
| | 77·0 | 1·091 | 0·0354 | 283 |
| β-Phenylpropionic acid ... | 130·0 | 1·023 | 0·0172 | 116 |
| | 49·7 | 1·047 | 0·0979 | 683 |

### Table IX.

*Nitriles of the Homologous Benzoic Acids at* 25°.

| | $D_{4°}^{25°}$. | $\eta^{25°}$. | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$ |
|---|---|---|---|
| Benzonitrile .. ......... ..... | 1·003 | 0·0125 | 122 |
| Phenylacetonitrile ............ | 1·015 | 0·0197 | 170 |
| β-Phenylpropionitrile ...... | 1·979 | 0·0477 | 322 |

Walden (*Zeitsch. physikal. Chem.*, 1911, **78**, 275) has recorded the absolute viscosities of benzonitrile and phenylacetonitrile as 0·0122 and 0·0193 respectively at 25°.

### TABLE X.

*Homologous Amines of the Benzene Series at* 25°.

| | $D_4^{25°}$. | $\eta^{25°}$. | $\frac{\eta \times 10^6}{\text{Mol. vol.}}$. |
|---|---|---|---|
| Aniline ........................ | 1·018 | 0·03740 | 410 |
| Benzylamine .................. | 0·9812 | 0·01596 | 146 |
| β-Phenylethylamine ......... | 0·9640 | 0·02490 | 198 |
| γ-Phenyl-*n*-propylamine ... | 0·9760 | 0·03570 | 240 |

Finally, we examined the similar series of homologous hydroxyl compounds at 25° and at 50°:

### TABLE XI*a*.

*Phenol and Phenylalkyl Alcohols at* 25°.

| | | | |
|---|---|---|---|
| Phenol .......................... | 1·070 | 0·0850 | 968 |
| Benzyl alcohol.................. | 1·045 | 0·05285 | 511 |
| β-Phenylethyl alcohol ...... | 1·023 | 0·07580 | 634 |
| γ-Phenyl-*n*-propyl alcohol | 0·995 | 0·156 | 1060 |

### TABLE XI*b*.

*The Same Compounds at* 50°.

| | | | |
|---|---|---|---|
| Phenol .......................... | 1·052 | 0·0337 | 377 |
| Benzyl alcohol ............... | 1·029 | 0·0260 | 248 |
| β-Phenylethyl alcohol ...... | 1·003 | 0·0319 | 262 |
| γ-Phenyl-*n*-propyl alcohol | 0·972 | 0·0521 | 373 |

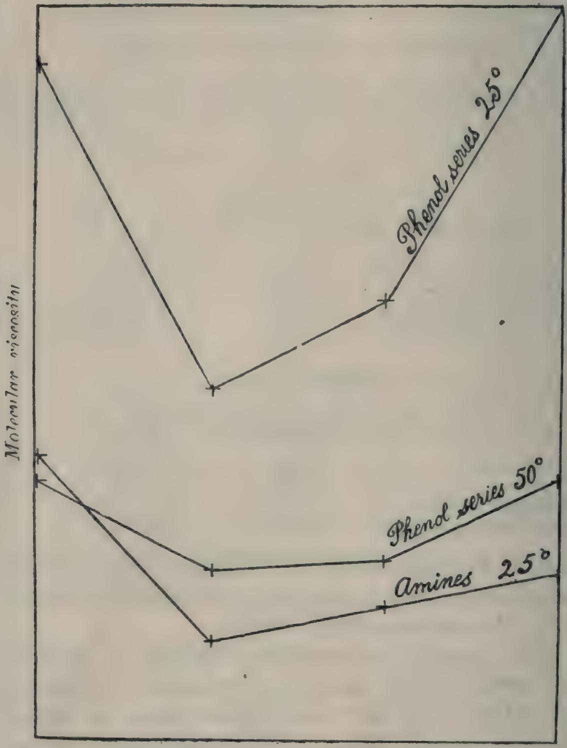
A comparison of these results with the preceding discloses at once certain resemblances and a number of marked differences, and is facilitated by the accompanying curve.

In the first place, if we confine attention in both classes of compounds—symmetrically and non-symmetrically substituted—to those series which have an unsaturated group in common, it is obvious that the general order of the viscosities at 25°, as exemplified by the relative positions of the corresponding curves, is the same for the chloro-, carbethoxy-, amino-, and cyano-derivatives. In addition, in the aromatic (non-symmetrically disubstituted) series, the curve connecting the viscosities of the corresponding aromatic hydrocarbons (in which compounds the second unsaturated radicle is replaced by a hydrogen atom) is beneath all the related curves. In other words, the order in which the curves arrange themselves in each of the two groups is not only the same, but is also approximately that of increasing unsaturation of the second unsaturated residue (R′), so far as can be judged from a general survey of the usual physical and chemical characteristics conferred on compounds by the substituents in guestion.

Moreover, in general, the first member of the series, containing two chemically adjacent unsaturated groups, possesses an enhanced viscosity compared with the values for the remaining members of the series.

Here, however, the resemblance between the two groups of curves ends, and further consideration of the aromatic group shows that the latter arrange themselves in two divisions:

FIG. 3.



*Molecular weight.*

(*a*) Those series which show a marked exaltation for the first (conjugated) member, namely, the hydroxy-, amino-, cyano-compounds and esters.

(*b*) In the second division of the aromatic series, which comprises the chloro- and hydrocarbon groups, no measurable depression occurs at the second member, and this is not unnatural, since, whilst the chlorine atom in organic compounds is generally supposed to possess but little residual affinity, the hydrocarbons contain no second unsaturated residue at all, and consequently the effects of conjugation are at a minimum in both cases.

Regarding the question in this light, and bearing in mind the general behaviour of compounds containing chemically adjacent unsaturated groups, it is natural to suppose that the separation of these groups leads to a falling off in any enhancing effect, but that such exalting influences again become apparent as the unsaturated residues gradually reapproach each other in space. It would have been most interesting to have examined the higher members in each series, but, as is well known, most of these have yet to be synthesised, whilst the difficulties of preparation and purification of the few which are known increase out of all proportion to their molecular weight.

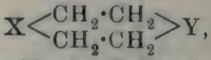
Nevertheless, we are able to point out the following consistent effects caused by the replacement of hydrogen by chlorine, the carbethoxy-group, the cyano-, amino-, and hydroxyl-residues on the curves connecting the viscosities of the members of the various homologous series:

(i) The relative positions of the curves are in the order given, that is, with one or two exceptions discussed below, the general order of increasing unsaturation of the second unsaturated group.

(ii) The slope of each curve is roughly determined by its relative position, and increases progressively as the second substituent becomes less saturated.

(iii) Correspondingly, the magnitude of the depression at the second member increases on passing up the series of curves in exactly the same order.

Most remarkable, however, is the fact that the well-defined exaltation characteristic of the substances of the general formula $R\cdot CH_2\cdot CH_2\cdot R$ is totally absent in the aromatic series we have studied. Two possible explanations suggest themselves in this connexion: from steric considerations it is likely that in view of the greater mass of the phenyl group the remaining (smaller) unsaturated radicle is not in the same spatial position with regard to that group in the compound $R\cdot CH_2\cdot CH_2\cdot Ph$ as the two (small) unsaturated residues are to each other in the symmetrical compounds $R\cdot CH_2\cdot CH_2\cdot R$. Another possibility raises the whole question of the mutual influence of two identical as compared with that of two different unsaturated radicles; is it possible that two identical unsaturated radicles, spatially proximate in the same molecule, should exert an exalting effect on a physical property, whilst two dissimilar unsaturated groups in the same relative configurations may depress the values for the same property?

Some recent work by Clarke (T., 1912, **101**, 1801) lends support to the supposition that such may be the case, for this author finds that the reactivity of compounds of the type  $X{<}\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}{>}Y$, where X and Y are two atoms possessing residual affinity, is promoted when X and Y are the same, but decreased when these are atoms of different elements.

### *General Conclusions.*

(1) We have examined the viscosities of a number of homologous series of compounds of the respective types $R\cdot[CH_2]_n\cdot R$ and $Ph\cdot[CH_2]_n\cdot R$, where R is a varying unsaturated radicle.

(2) In both series the general order of the molecular viscosity rises when R is varied in the order: chloro-, carbethoxy-, amino-, and cyano-radicles.

(3) In both series the initial member, containing two chemically adjacent unsaturated groups, has been found to possess an exalted molecular viscosity.

(4) In the symmetrical series $R\cdot[CH_2]_n\cdot R$ the members represented by $R\cdot CH_2\cdot CH_2\cdot R$ possess an enhanced value for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$, but this is not the case in the phenyl group of compounds.

(5) In the latter group of compounds the anomaly of the initial member is in general very pronounced, and is followed by an equally well-marked depression in the case of the viscosity of the second member, the values thereafter rising somewhat rapidly; the extent of the depression, the relative slope of the curves, and the relative positions of the curves are in the order: chloro-compounds, esters, amino-, cyano-, and hydroxy-compounds.

(6) The series examined afford undoubted evidence of the strong mutual influence of two unsaturated groups upon viscosity, not only when the radicles concerned are adjacent in the molecule, but also when they may be supposed from common steric considerations to approach one another in space.

(7) In addition, we have obtained indications of the varied influences exerted by combinations of two similar, and, on the other hand, of two dissimilar radicles, the effects in the latter case depending to all appearance on the relative degree of unsaturation of the component radicles; our data, however, do not permit us to define the latter variations more particularly.

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# XXI.—*An Attempt to Harmonise, Qualitatively, the Relation between Temperature and Rotation for Light of all Refrangibilities of Certain Active Substances, both in the Homogeneous State and in Solution.*

By THOMAS STEWART PATTERSON.

IT would probably be fairly generally conceded that the work of the past hundred years on optical activity, instead of reducing has tended to increase the difficulty of the subject, and to render it, as time goes on, less, rather than more, capable of generalisation, because of the great diversity of the causes the effects of which have first to be discovered and then brought into relationship. It has become clear, of course, that optical rotation, which depends, in the first place, on the chemical nature of the active substance, depends also on the temperature and on the wave-length of the light used. Considering the large number of active compounds now known, the generalisation of this field alone constitutes an immense problem, but if the active substance be mixed with an indifferent medium, there must further be taken into account the nature of the solvent and the concentration, whilst the temperature and colour of light must be considered afresh, since their influence may be entirely different in the new circumstances from what obtained for the homogeneous compound.

The number of variables is thus large, and the chief reason why no really comprehensive scheme has been possible is that the connexion between the rotation and these other variables has seldom been studied in a thoroughly systematic manner.

In regard to one of these variables, and that, perhaps, the most important, the course of events was distinctly unfortunate, for although Biot showed, in some of his later papers, that the rotation of an active compound is not independent of temperature, the importance of this factor, on account of his earlier work, was greatly underrated by subsequent investigators, with the result that much of the experimental material they accumulated is practically useless for purposes of generalisation. In the last twenty years, however, and chiefly owing to the example of P. F. Frankland, the examination of an active compound over as wide a range of temperature as possible is gradually becoming, as it ought to be, a matter of ordinary routine.

The discovery of the first example of what seems likely to prove an important phenomenon in this connexion was made by Frankland and Wharton (T., 1896, **69**, 1587) some sixteen years ago, when they found that ethyl dibenzoyltartrate in the homogeneous condition shows a distinct maximum negative rotation at a temperature of 60°, whilst in a previous paper (T., 1896, **69**, 1309) these authors give data which strongly indicate the existence of maximum negative rotations, at temperatures of about 20°, for methyl *o*-toluoyl-, ethyl *o*-toluoyl-, and ethyl *m*-toluoyl-tartrates. Some years afterwards Grossmann and Pötter (*Ber.*, 1904, **37**, 84) found that ammonium and sodium molybdanyldimalates, at several concentrations, show maximum rotations at 35° and 50° respectively, and about the same time Patterson (T., 1904, **85**, 1116) found maxima in the temperature-rotation curves for solutions of sodium and potassium tartrates, of potassium methyl, potassium ethyl, and potassium *n*-propyl tartrates, and probably also in solution of methyl and ethyl tartrates. Then Patterson and Taylor (T., 1905, **87**, 33) discovered an instance strictly analogous to the ethyl dibenzoyltartrate of Frankland and Wharton while examining menthol, which was found to have a maximum negative rotation of −77·94° between 58° and 59°. Some years previously Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 176), assuming that the relationship between rotation and temperature of ethyl tartrate may be represented by a parabolic equation, deduced from his results for this ester—as well as for methyl tartrate and propyl tartrate—a maximum specific rotation at a temperature of 149°, and Patterson, a few years afterwards (T., 1908, **93**, 1843), showed that a maximum does exist, but at a temperature of 175°, and, further, that when the ester is dissolved in nitrobenzene and a number of other similar solvents, the maximum persists, and is observed to move towards a higher value and a lower temperature with increasing dilution. Later Patterson and McDonald (T., 1909, **95**, 323) found that a $p=10$ solution of ethyl tartrate in quinoline has a minimum rotation of 16° at a temperature of about 94°. Again, Patterson and Miss Stevenson (T., 1910, **97**, 2121) pointed out the existence of maxima in resorcinol-, quinol-, *m*-nitrophenol-, etc., solutions of ethyl tartrate; Pickard and Kenyon (T., 1911, **99**, 52, footnote) record the occurrence of minimum rotations for methyl-*n*-butyl- and methyl-*n*-octyl-carbinols at about 125° and in six other alcohols (T., 1912, **101**, 626); Cohen (T., 1911, **99**, 1060) discovered a maximum negative rotation for menthyl-*o*-iodobenzoate at about 60°, whilst Patterson and Davidson (T., 1912, **101**, 374) observed that ethyl, *iso*butyl, and probably also methyl, di-trichloroacetyltartrates show minima in their temperature-rotation curves, and that these minima persist in solution in nitrobenzene and move with increasing dilution towards a lower temperature and a lower value.

Thus a number of homogeneous substances and some of them also in solution present the phenomenon of a maximum or minimum rotation at a definite temperature, and, if the importance of singular points in the mathematical treatment of curves is remembered, it would seem probable that such singular points as those mentioned will ultimately prove to be of the greatest value in regard to the theory of optical activity. For the great difficulty which has always been found in discussing the influence of temperature on rotation is that no criterion exists meanwhile to justify a decision as to which parts of two curves represent the optical properties of the compounds in really comparable conditions. The great merit therefore of a point of maximum rotation is its recognisability; for, if it be assumed that a point of maximum rotation indicates that condition of a substance in which one of the groups attached to the asymmetric atom attains to a maximum influence, then a maximum rotation for another closely related substance may legitimately be taken to represent its optical properties in, at the very least, a similar condition.

### *The Rotation of Homogeneous Compounds.*

From this point of view further information in regard to maximum rotations such as described above seemed desirable, the immediate objects of the present investigation being, firstly, to ascertain whether the rotations of other simple esters of tartaric acid also reach maximum values, and, secondly, how these maxima, if they exist, are related to each other. In order to test these points the ethyl,* *n*-propyl, *sec*.-propyl, allyl, *iso*butyl, *iso*amyl, *sec*.-octyl, and benzyl esters of tartaric acid, of which the fourth and the last appear to be new, have been examined, as regards rotation, over a considerable range of temperature. The experimental data are recorded at the end of the paper, where also some points arising out of these data, but not directly concerned with the main purpose of the investigation, are referred to.

Fig. 1 reproduces the curves for the molecular rotation of these esters, and, on the whole, the graphs are obviously alike in general characteristics,† but it will be clear that, even for such closely similar substances as these, the institution of comparisons between the rotation values at any one given temperature could hardly be expected to yield satisfactory results. The data for the esters at 20° would not be in the same sequence as at, say, a temperature of 180°. At the former temperature, allyl tartrate has a higher rotation than has *iso*amyl tartrate, whereas at the latter the reverse is the case, and other similar examples will be obvious from the figure.

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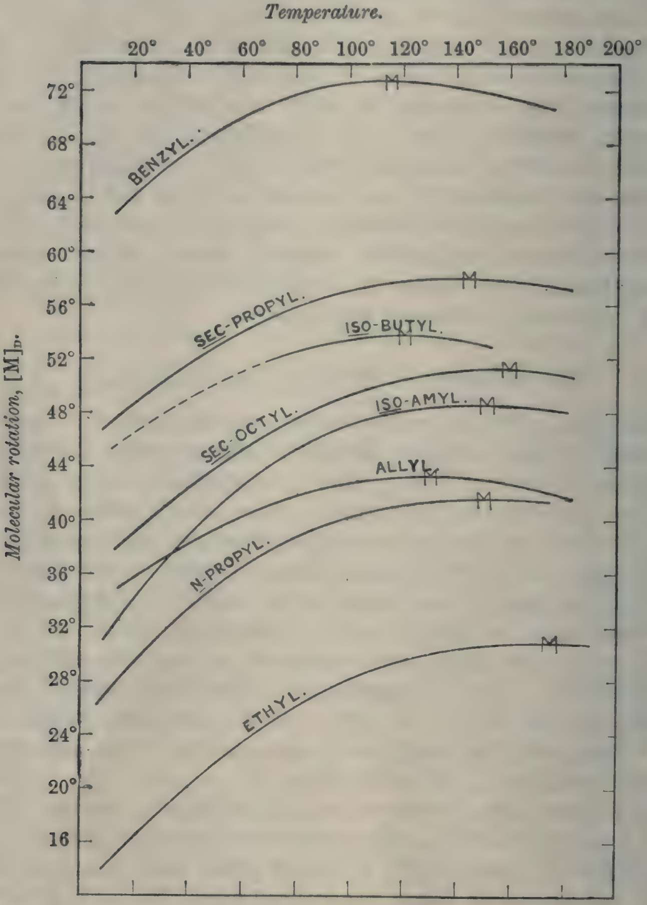
* The maximum rotation of methyl tartrate occurs at a temperature a little too high to be estimated by the apparatus at the disposal of the author.

† It should be noted that the maximum in observed rotation occurs at a lower temperature than the maximum for molecular rotation.

FIG. 1.

*Temperature-rotation curves for various esters of tartaric acid.*



As regards the values of the maximum rotations, it will be clear, in the first place, that they do not all occur at the same temperature. The actual details will be found in the following table. All that need be said in the meantime regarding these data is that, roughly, the value of the maximum molecular rotation is higher the lower the temperature at which it occurs.

### Table I.

*Maximum Rotation Values and the Temperatures at which they occur for Certain Esters of Tartaric Acid.*

| Ester. | Maximum $\alpha_D$. | $T$. | Maximum $[\alpha]_D$. | $T$.* | Maximum $[M]_D$. |
|---|---|---|---|---|---|
| Diethyl tartrate.. | +15·93° | 148·0° | +15·0° | 175° | 30·9° |
| Di-*n*-propyl tartrate | 18·3 | 115·0 | 17·8 | 150 | 41·65 |
| Di-*sec.*-propyl ,, | 25·2 | 93·0 | 24·8 | 144 | 58·03 |
| Di-*iso*butyl ,, | 20·65 | 93·0 | 20·57 | 120 | 53·9 |
| Di-*iso*amyl ,, | 16·1 | 118·5 | 16·8 | 151 | 48·72 |
| Di-*sec.*-octyl ,, | 12·4 | 122·5 | 13·76 | 160 | 51·46 |
| Diallyl ,, | 20·75 | 100·0 | 18·8 | 130 | 43·24 |
| Dibenzyl ,, | 26·1 | 88·0 | 22·06 | 115 | 72·80 |

It has already been remarked that the effect of temperature on rotation is thus very difficult to trace; for example, it has often been found that two compounds intimately related chemically show an exactly opposite behaviour as regards the influence of temperature change on their rotations. A considerable number of examples of this behaviour could be cited, but one will probably suffice. The rotation of ethyl diacetyltartrate (McCrae and Patterson, T., 1900, **77**, 1106) increases with rise of temperature; that of ethyl di-monochloroacetyltartrate increases by about the same amount, whilst that of ethyl di-dichloroacetyltartrate is almost unchanged by alteration of temperature from 15° to 100° (Frankland and Patterson, T., 1896, **73**, 207), but that of ethyl diphenacetyltartrate diminishes rapidly as the temperature rises. There is obviously, underlying this behaviour, a distinct regularity, but it is one which cannot readily be expressed in a general manner.

In considering the very similar case of the dialkyltartrates, the potassium alkyltartrates, and dipotassium tartrate (Fig. 2), all in dilute aqueous solution, the author suggested that the rotation-temperature curves represented, "in the case of the dialkyltartrate, only one limb, the descending one; for the potassium alkyltartrates, both limbs, and for potassium and sodium tartrates, again only one limb, the ascending one, of curves which are in all three cases of a similar kind" (T., 1904, **85**, 1142). In other words, the temperature-rotation curves of chemically similar substances are of the same type, but the maximum does not occur in each at the same temperature. For one compound it may lie towards a low temperature outside the range of the experiments, in which case the temperature-coefficient of the rotation will be negative, that is, the rotation will decrease as the temperature rises. For another compound the maximum may lie towards a high temperature outside the range of the experiments, when, of course, the temperature-coefficient at the ordinary temperature will be positive, the rotation will increase with rise of temperature.

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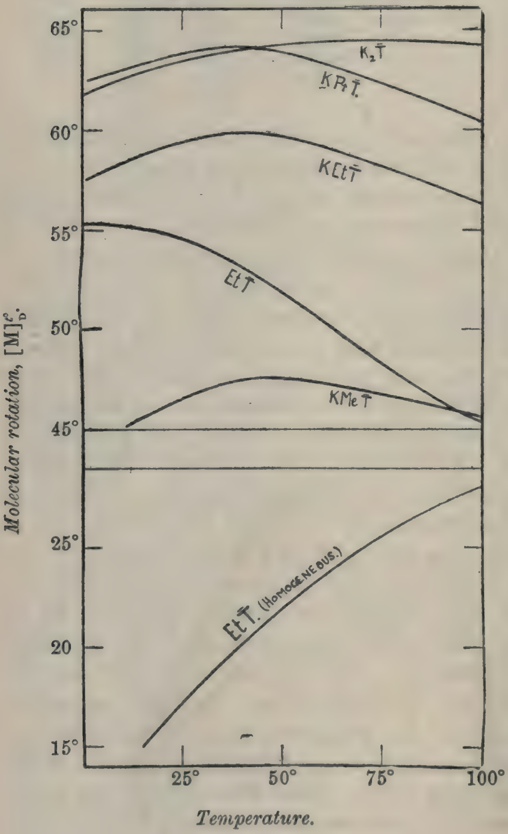
* The maxima for specific, and molecular, rotation occur, of course, at the same temperatures.

For the homologous alkyl esters of tartaric acid, the curves of which are represented in Fig. 1, the temperature of maximum rotation does not vary much; for compounds related to each other, as are diethyl tartrate, ethyl potassium tartrate, and dipotassium tartrate, the difference is much greater. The temperature of maximum molecular rotation for diethyl tartrate lies at 175°; for homogeneous potassium ethyl tartrate it would lie in the neighbourhood of 70° (T., 1904, **85**, 1123, Fig. 5), and for dipotassium tartrate at a much lower temperature, which cannot even be roughly estimated (*ibid.*, p. 1119, Fig. 2). The conception, therefore, of the existence of a maximum rotation outside the temperature range of the experiments is sufficient at once to account for the occurrence, within the ordinary range of temperature, of opposite temperature-coefficients for analogous compounds.

FIG. 2.

*Temperature-rotation curves for various substances in aqueous solution. p=5.*

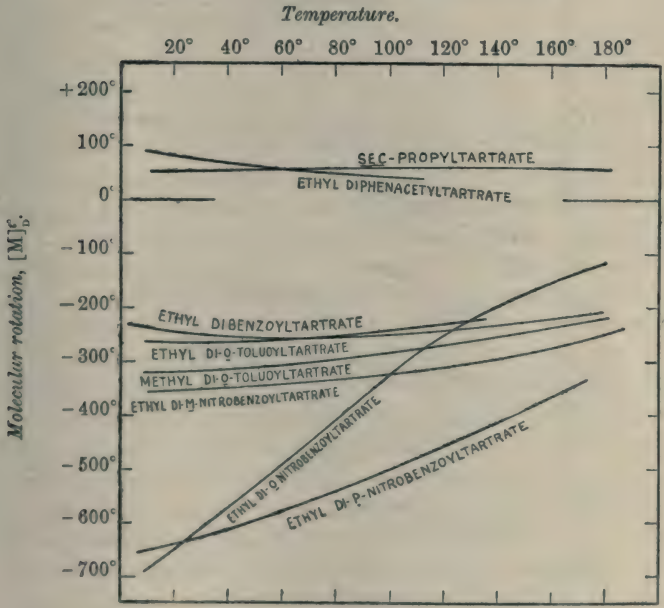


Now, as has already been mentioned, the prediction of maxima is a necessary consequence of the assumption that the temperature-rotation curve of an active compound is of parabolic form, but since the parabola is a symmetrical curve, it would also follow that the two limbs of the temperature-rotation curve should be identical in shape,* and that the rotation should diminish constantly on both sides of the maximum value. It is of some interest, therefore, to ascertain, if possible, whether these are really parabolas.

Unfortunately the range of temperature over which rotation can be examined is usually comparatively short; at high temperatures there is the possibility of decomposition of the substance or the difficulty of finding a suitable tube to contain it, and at low temperatures the compound is likely to solidify. Even the examination of solutions of active compounds at low temperatures will present considerable difficulty, and for these reasons it is only possible, in the meantime, to progress by piecing together such evidence as appears to bear on the question.

FIG. 3.

*Temperature rotation curves for various esters.*



It is a little doubtful whether any of the temperature-rotation curves hitherto obtained are sufficiently extensive to allow of mathematical determination of their form, but a considerable amount of cumulative, if slightly indirect, evidence can be adduced in regard to this question.

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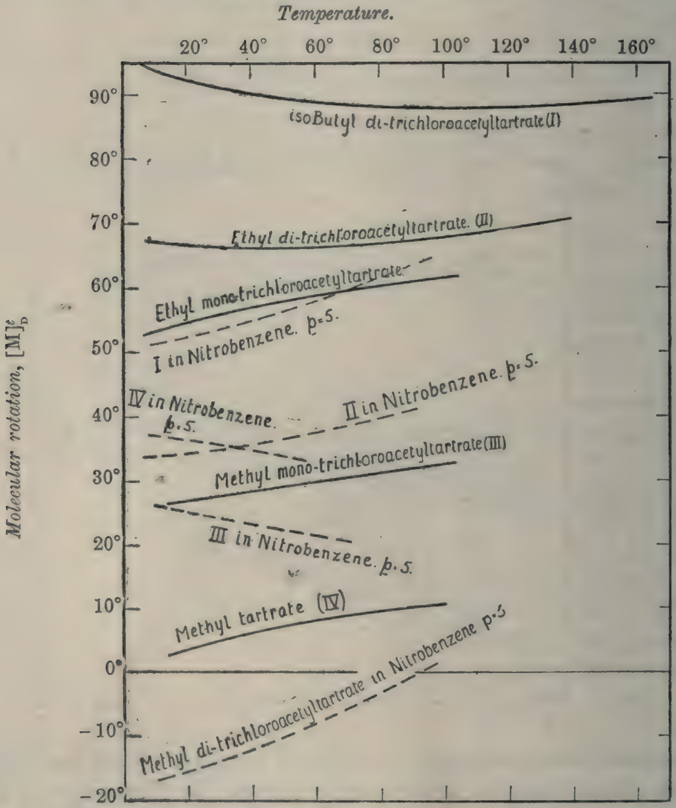
* Neglecting the slight alteration of form introduced by the shape of the density curve.

Some relevant matter is represented by the curves of Fig. 4, which have been plotted from data obtained by Patterson and Davidson (T., 1912, **101**, 374). The uppermost curve is that for homogeneous *iso*butyl di-trichloroacetyltartrate, and, as will be

FIG. 4.

*Temperature-rotation curves.*



observed, a distinct minimum occurs at 105° of $[M]_D + 88°$. The curve for ethyl di-trichloroacetyltartrate also shows a minimum at a temperature of 54°, and having the value $[M]_D + 66°$. In this case, therefore, the minimum rotation appears to move towards a higher value and a higher temperature as the series is ascended.

It is of great interest to compare these curves, in both of which the maximum rotation actually appears, so that its variation can be traced, with some of the curves of Fig. 3, which mostly represent data obtained by P. F. Frankland and his pupils, and serve admirably to exhibit the very great effect that change of temperature may exert.

The curves shown refer to a number of compounds fairly intimately related to each other. The scale of the rotations is here very small, as will readily be apparent from the appearance of the graph for *sec.*-propyl tartrate, which is included for comparison; the curvature in this instance, although so obvious in Fig. 1, is little more than perceptible.

The behaviour of ethyl dibenzoyltartrate has already been referred to, and is of especial interest. It shows a maximum negative rotation of −258° at a temperature of 63°. The other graphs, on the lower part of the diagram, give the results of observations by Frankland and Wharton (T., 1896, **69**, 1309, 1583) and Frankland and Harger (T., 1904, **85**, 1571). It is clear that the curve for ethyl dibenzoyltartrate is closely resembled by that for ethyl di-*o*-toluoyltartrate, and it seems almost absolutely certain that just as the maximum positive rotation of the simple alkyl tartrates of Fig. 1 moves towards a lower temperature and a greater value, and the minimum rotation of the di-trichloroacetyltartrates (Fig. 4) moves to a higher value and a higher temperature in passing up the homologous series, so the maximum negative rotation of ethyl dibenzoyltartrate will have its analogue in a maximum negative rotation for ethyl di-*o*-toluoyltartrate, but at a lower temperature and a greater negative value. Similarly, the slopes of the curves for ethyl di-*m*-nitrobenzoyltartrate and ethyl di-*p*-toluoyltartrate suggest maximum negative rotations at still lower temperatures. The curve for ethyl di-*o*-nitrobenzoyltartrate is the most remarkable of all. The very high negative rotation diminishes with surprising rapidity as the temperature rises, the slope of the curve suggesting a maximum negative rotation at a very low temperature. The most important thing about this curve, however, is that it appears to have a point of inflection somewhere about 80°, the curvature above that temperature being certainly the opposite of that of the graphs for the analogous compounds. The form of this part of the curve is thus similar to that of ethyl tartrate between 0° and 150°, and therefore the possibility of the rotation of this compound rising* to a maximum is suggested, and from the similarity of the set of curves there would be, with almost equal probability, a maximum in the curve for the analogously constituted ethyl di-*p*-nitrobenzoyltartrate at a higher temperature, and in the same way, maxima may be anticipated in each of these curves at successively higher temperatures. Further very important evidence is to be found in the admirable work of Pickard and Kenyon (T., 1911, **99**, 45; 1912, **101**, 620), their second paper containing two most interesting diagrams, which merit careful examination. It may particularly be noticed that maxima occur in the curves (*loc. cit.*, p. 623) for *n*-hexyl-, *n*-octyl-, and *n*-decyl-*sec.*-propylcarbinol, and that, in addition, there is a point of inflection at higher temperatures, so that the curves appear to be falling to reach a minimum such as becomes much more obvious in the curves of the diagram on p. 626. Here a decided point of inflection for ethylmethylcarbinol is still apparent in *n*-propylmethylcarbinol, but develops into a minimum in *n*-butylmethylcarbinol, a minimum which gradually moves towards a higher temperature as the homologous series is ascended. Thus the variation of the rotation of an active compound with change of temperature may be, and very probably is, a *periodic* phenomenon—doubtless irregularly periodic—and several maxima and minima may be expected to occur as one or other of the groups attached to the asymmetric atom exerts a preponderating influence. Some further evidence bearing on this point will be found on p. 161.*

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* That is, the negative rotation becomes less. It would probably be best to refer to the turning points of the curves for genetically-related compounds, as maxima or minima, irrespective of the actual sign of the rotation.

In passing from a given substance to one of a closely analogous type, the shape of this irregularly periodic curve alters slightly, because the temperature, at which one of the groups attached to the asymmetric centre becomes predominant, is a little different; the one curve is somewhat retarded or advanced as the case may be, on the other, whilst the rotation produced, the amplitude, also changes by a small amount.

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* Since this was written, there has appeared a paper by Frankland, Carter, and Adams (T., 1912, **101**, 2470) which contains a diagram representing the optical behaviour of a splendid series of thirteen acidyl derivatives of methyl tartrate, of the utmost interest and importance in connexion with the views developed here. Methyl *o*-iodobenzoyltartrate has a comparatively low rotation which varies in such a way that there is a distinct maximum negative rotation at a temperature of about 80°. The corresponding bromo-derivative (for which the curve is not quite so satisfactory) has a greater negative rotation and a maximum occurring at about 40°. The curve for the *o*-chloro-compound shows a higher rotation with a maximum at about 50°. It appears, therefore, making some allowance for the curve of the bromo-compound, that the maximum passes to a lower temperature as the value of the rotation increases, and that this is so is very fully borne out by the appearance of the other curves shown on the diagram. The curves for the benzoyl and the *o*-toluoyl derivatives intersect in such a way as to indicate that the former is retarded on the latter. A further very important thing is to be noticed also in the diagram, namely, that the curves for the *m*-toluoyl and the *p*-toluoyl esters have the opposite curvature from the other graphs. They must almost certainly show a point of inflection in the neighbourhood of 130°, just as has been suggested for the curve for ethyl *o*-nitrobenzoyltartrate in Fig. 3 of this paper. Frankland, Carter, and Adams point out that there is a tendency for the rotation of the substances they have examined to become equalised at high temperatures, but it seems highly probable to the present writer that the curves will intersect in such a manner that at some higher temperature, say from 400° to 500°, the sequence of the rotations would be just the opposite of what it is at, say, 60°.

As has been said, no satisfactory generalisation can be arrived at regarding the curves of Fig. 1, by a consideration of rotation values for any one temperature, and it is therefore of interest to note that the ideas so far developed seem to render possible a description, at least, of the behaviour of the compounds, which shall be independent of temperature, and this in terms of the two variables phase and amplitude; thus the curve for *n*-propyl tartrate is somewhat advanced on that for ethyl tartrate, since its maximum is at a lower temperature, and, at the same time, its amplitude is greater. Similarly, the curves for allyl tartrate and for *iso*butyl tartrate are successively in a more advanced phase, again with an increase in amplitude. The amplitude for *sec.*-propyl tartrate is still greater, but the curve is retarded on that for *iso*butyl tartrate, and so on, these statements describing the behaviour of the substances through the whole range of temperature examined.

It is to be observed that the sweep of most of these curves appears to be very similar, so that the period or wave-length of the temperature-rotation vibration—which, not quite in conformity with ordinary usage, may be described for convenience as the distance between a maximum and a minimum value—is possibly nearly the same for these esters, but, of course, in the meantime no definite conclusion can be arrived at in regard to this point. The only graph which does not appear to have the same sweep as the others is that for *iso*amyl tartrate, but this ester was not quite pure (see p. 175), a fact which may readily account for the slight peculiarity.

The same kind of treatment can be applied to the curves of Fig. 3, which may be referred to in connexion with the problem of position isomerism and rotation. It has been shown by P. F. Frankland that in a large number of cases the rotatory power of a set of isomerides is in the order ortho, meta, para; and that, if these are derivatives of benzoyl, the benzoyl compound itself falls, in respect of rotation, between the ortho- and the meta-derivatives. This is a regularity which even persists over a fairly wide range of temperature in many instances, but the graphs of Fig. 3 show how such a rule as this may be completely upset by alteration of temperature. At 160°, for example, we find, for some of the compounds represented, the sequence, *o*-nitrobenzoyl, benzoyl, *m*-nitrobenzoyl, *p*-nitrobenzoyl, which is thus in complete accordance with Frankland's rule. At 110°, however, the sequence is: benzoyl, *o*-nitrobenzoyl, *m*-nitrobenzoyl, *p*-nitrobenzoyl, whilst at 40° and at 20° still other sequences are found. Since, therefore, the sequence varies for each of these different temperatures, that for any particular temperature can only have a very limited application or interest.

The whole behaviour of the compounds is summed up, however, in a qualitative sense, for any temperature, in the statement that the phase as well as the order of magnitude of the amplitude is in the sequence:

Ethyl di-*o*-nitrobenzoyltartrate,
Ethyl di-*p*-nitrobenzoyltartrate,
Ethyl di-*m*-nitrobenzoyltartrate,
Ethyl dibenzoyltartrate,

the substance first mentioned being in the most advanced phase and having the greatest amplitude.

These views can only be applied qualitatively in the meantime, and it is doubtful, in spite of all the data that have been collected, whether the experimental material is sufficiently comprehensive, in the sense of including as many of the variables as is necessary, to make it desirable to attempt a quantitative treatment of the subject. At present it need only be said that a set of graphs such as those of Fig. 1 or Fig. 3, assuming them to be periodic, suggest a rough resemblance to a series of sine curves, and possibly, as a first approximation, an expression of the form:

$$a = e^{-at} \sin(bt + c),$$

the graph of which is a curve of changing amplitude, may be proposed—mainly as a concrete example and for purposes of illustration—to represent the relation between temperature and rotation. Of the parameters in this expression, *a* changes the amplitude, *b* changes the period, whilst *c* alters the phase.

One other and rather important point must be referred to, namely, the relationship as regards rotation between compounds of different type. It seems to the author that there is now some hope that by a very complete examination of the rotation of active compounds it may be possible to discover the connexion between rotation and chemical constitution, even of substances differing as do glyceric acid and tartaric acid, but that is, in the meantime, merely a pious aspiration. The simpler problem, however, of the relationship between the curves for the various esters of one acid, say, tartaric acid, may be considered. The temperature-rotation curve for tartaric acid, which, very unfortunately, cannot actually be determined, may be regarded as a fundamental graph for a large class of compounds. From data obtained by extrapolation from observations on concentrated aqueous solutions, and from analogy to the behaviour of the simple alkyltartrates, it is practically certain that the homogeneous acid will have a negative rotation at the ordinary temperature, and that this will rise with increase of temperature to reach a maximum of comparatively low value at a temperature in the neighbourhood of 200°. Substitution of the acidic hydrogens by alkyl groups—a slight change—shifts the maximum rotation to a lower temperature as the alkyl group increases in mass—at least, up to a certain point—and at the same time the amplitude increases also (Fig. 1), but the data are not full enough to allow of a complete statement even in this one case. We do not know what happens at temperatures higher or lower than those hitherto investigated. On substituting the hydroxylic hydrogens of one of these esters, say, ethyl tartrate, by acyl groups, a greater change occurs, the nature of that part of the curve within the range of ordinary temperatures alters, since the graphs for the alkyltartrates, Fig. 1, on the one hand, and those for the acyl derivatives, Figs. 3 and 4, on the other, are of different shape. The former show a temperature of maximum rotation, and the latter a temperature of minimum rotation, and this minimum again moves about to various temperatures and rotation values as slight changes are made in the substituting groups. Now if both the curves for the alkyltartrates and those for the acyl derivatives were parabolas there could hardly be any hope of deriving them from one common origin. If, however, they are periodic, the problem appears to be much simpler and capable of solution, for it seems not unreasonable to suppose that the very considerable change in constitution from ethyl tartrate to ethyl di-trichloroacetyltartrate, for instance, may have the effect of displacing the ethyl tartrate curve—in the same way that the substitution of a propyl group for the ethyl group would displace it, but to a very much greater extent—towards a higher or lower temperature so as to bring into view a minimum which would only appear in the ethyl tartrate curve within a region of temperature not easily explored.

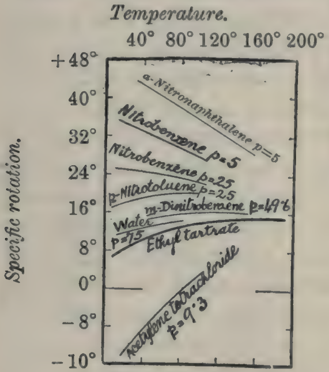
### *Rotation in Solution.*

That the temperature of maximum rotation may play in the future an important part in connexion with the rotation of homogeneous substances will, it is hoped, be evident from what has already been said; an attempt will now be made to show that it is of equal importance in regard to the phenomena of rotation in solution, and here again the great value of a maximum is the fact that it can be easily recognised. The maximum indicates a condition of the substance in which a certain influence—or influences—attains to a maximum, and then declines again or is outweighed by other influences, this taking place under the inter-molecular forces—the forces which produce liquefaction—at play in the compound in these particular circumstances.* If now the active substance be mixed with an indifferent solvent, the inter-molecular forces change so that the internal pressure to which the active compound is subjected assumes a different value. Under this new pressure a different temperature is required to produce that state of the molecule in which one of the groups attached to the asymmetric atom reaches its maximum preponderance, and since at that new temperature the molecule as a whole will have changed—in volume, for instance—the maximum rotation will have a value other than that found for the homogeneous compound, unless, of course, the internal forces happen to be just the same as before, when the temperature of maximum rotation should also be the same. As the solution becomes more and more dilute the internal forces gradually alter, and the temperature of maximum rotation suffers a corresponding change.

FIG. 5.

*Influence of temperature on rotation in solution.*

*Ethyl tartrate in various solvents.*



Previous work has shown (T., 1908, **93**, 1843) that when ethyl tartrate is mixed with a solvent, such as water or nitrobenzene, which raises its rotation at ordinary temperatures, the maximum rotation passes towards a lower temperature, but takes on a higher value as the solution becomes more dilute, and, further, that the extent to which the temperature of maximum rotation is lowered is almost directly proportional to the rise in the value of the rotation. This will be clear from the curves of Fig. 5. It will be observed that in a solvent such as acetylene tetrachloride, $p = 9·3$, which, at 20°, has a powerful depressing influence, the rotation rises rapidly with increase of temperature, whilst in a solvent like α-nitronaphthalene, $p=5$, which greatly raises the rotation of the ester, increase of temperature diminishes the rotation with almost equal rapidity. Other solvents or the same solvents at intermediate concentrations, produce effects lying between these extremes, in such a manner that, roughly speaking, the whole series of curves gives the impression of a gradual variation of some property irrespective of the chemical composition of the solvents. If a solution in water and one in nitrobenzene have a certain rotation at some given temperature, then the temperature-rotation curves of the two solutions will be practically identical, although the concentrations may be entirely different. According to the author's working hypothesis, the internal forces against which the molecule has to expand on heating are the same or almost so, the optical behaviour being then naturally very similar. Nevertheless, although, broadly speaking, this is the case, there are minor irregularities, as will be seen on inspection of the diagram on p. 1846 of the *Transactions* for 1908.

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* In the author's view, it is probable that the rotation of the free molecule of an active substance—that is, in the state of vapour—would also show maxima and minima, although this has not been experimentally verified. In the liquid condition the active molecules are subjected to new and powerful forces, and therefore the maximum rotation would probably not occur at the same temperature for the liquid as or the vapour

It is to be surmised that if ethyl tartrate be dissolved in a liquid of depressing influence such as acetylene tetrachloride, the maximum will move to a higher temperature, but will at the same time assume a lower value than characterises the maximum for the homogeneous ester, and that this tendency will become more and more marked as the dilution increases, a point which will be referred to later on (p. 171). It may be noticed that ethyl tartrate seems to fall into line with the other indifferent liquids as a solvent for itself.

The influence of solvents on other rotation maxima is of a similar character to that just described. Very decided maxima were found in the temperature-rotation curves for aqueous solutions of potassium methyl tartrate, potassium ethyl tartrate, and potassium *n*-propyl tartrate, and these maxima move in a very distinct and interesting manner towards a lower temperature and a higher value as the solutions become more dilute, just as does the maximum for ethyl tartrate on dilution with water, but the displacement of the maximum is not so great (see Figs. 4, 5, and 6, T., 1904, **85**, pp. 1121, 1123, 1125). In Fig. 2 of the present communication the curves for $p=5$ solutions of these compounds are shown, and it will be noticed that in passing from one to the other of these substances in aqueous solution the maximum rotation again moves towards a lower temperature and a higher value, just as is seen from Fig. 1 to be the case amongst the homogeneous alkyl esters of tartaric acid.

It is important now to consider the effect of solution on the critical points of other curves, some interesting information being represented in Fig. 4 in regard to the minima in the curves for ethyl di-trichloroacetyltartrate and *iso*butyl di-trichloroacetyltartrate (Patterson and Davidson, T., 1912, **101**, 377).

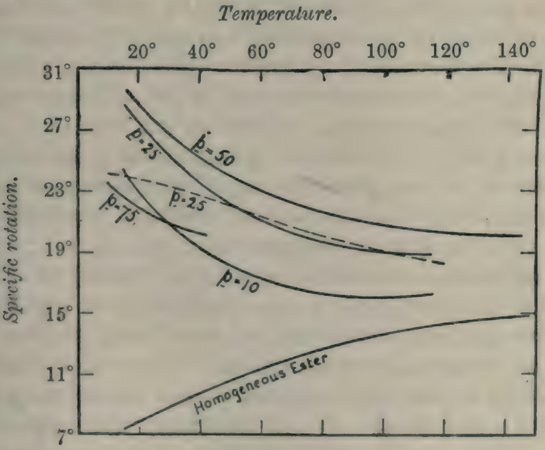
The rotation of both these esters is much depressed by solution in nitrobenzene (broken lines), and from the appearance of the curves and what has already been said, it may be regarded as almost absolutely certain that the minimum value of the rotation merely moves to a lower value and a lower temperature, just as the maximum rotation of ethyl tartrate has been observed to move towards a higher value and a lower temperature by dilution with nitrobenzene.

In regard to the influence of nitrobenzene as a solvent, methyl tartrate is closely analogous to ethyl tartrate. The rotation of homogeneous methyl tartrate is shown in Fig. 4. The maximum rotation has not actually been determined, but it must lie about 180° or perhaps a little higher. When dissolved in nitrobenzene ($p=5$), the ester has a high rotation, which diminishes on heating, so that in such a solution the maximum rotation has already passed to a temperature somewhere below zero; thus the minimum rotation of the di-trichloroacetyl esters is depressed and moved towards a lower temperature, whilst the maximum rotation of the simple esters is raised and also moved towards a lower temperature, when the compounds are examined in nitrobenzene solution. With the behaviour of these esters it is now most interesting to compare that of methyl mono-trichloroacetyltartrate, which, chemically, stands midway between them. The rotation of the homogeneous ester increases as the temperature rises, almost linearly (Frankland and Patterson, T., 1898, **73**, 186), but from analogy to the corresponding graph for ethyl mono-trichloroacetyltartrate, which shows a distinct curvature, it is to be expected that both would tend towards a maximum at a fairly high temperature. The curve representing the behaviour of a nitrobenzene solution of the methyl ester on heating is shown on the diagram. The value of the rotation is little altered, but the temperature-coefficient is the opposite of what it is in the homogeneous ester. The rotation diminishes on heating, and it may reasonably be concluded that in this case again the maximum for the homogeneous ester is moved towards a lower temperature by solution in nitrobenzene, but without any great alteration of value. Thus, in a very broad and general sense, the influence of solution in nitrobenzene on the rotation of all these esters is of just the same character; the curve for the homogeneous ester is, as a whole, displaced towards a lower temperature, towards the left of the diagram, and by nearly the same amount, the actual value of the rotation being lowered or raised or not much altered as the case may be, presumably according to the chemical nature of the active compound. If, then, we may regard these temperature-rotation curves as periodic, the effect of solution is to change, in the first place, the phase, and also the amplitude, of what may be called the vibration. And, further, since the sweep of these curves, both for the homogeneous esters and for their solutions, is, so far as can be judged, very similar, it may be concluded that the period of the vibration is, in practically all these instances, nearly the same.

The conception which the writer has attempted to develop in this paper bears in a very interesting manner on some results

FIG. 6.

*Ethyl tartrate in quinoline (full lines), and in water (broken line).*



which, at the time they were obtained, were difficult to understand or to correlate with any other phenomena. It was found that solution in water raises the rotation of ethyl tartrate, at the ordinary temperature, to a considerable extent, and that, as is usual in such cases, the rotation diminished with rise of temperature (T., 1904, **85**, 1129, 1130). It was also noticed, however, that the curves for fairly dilute solutions, in addition to suggesting the passing of a maximum rotation to a lower temperature as the dilution increases, also exhibit a point of inflection at a temperature somewhere about 60°. This will be seen from the curve for water, $p = 25{\cdot}034$, which is reproduced in Fig. 6. Then, later, it was observed by Patterson and McDonald (T., 1909, **95**, 323) that the influence of quinoline as a solvent on the rotation of ethyl tartrate differed considerably from anything previously recorded. The curve, even for a $p=50$ solution, starting from a high value at low temperatures, falls rapidly as the temperature increases, in such a way as to be convex with regard to the point of origin of the figure, and tending towards a minimum value in the neighbourhood of 100°. These curves, also, are shown in Fig. 6. It will be noticed that even the curve for a $p=75$ solution is convex with respect to the point of origin of the diagram, and it is therefore to be surmised that the maximum rotation of ethyl tartrate passes very rapidly towards a low temperature, on solution in quinoline, just as is the case in nitrobenzene and water and many other solvents. Only a few observations were made with the $p=75$ solution, but it is clear that the behaviour of a $p=50$ solution shows a gradual advance on that of the $p=75$ solution, of a similar character to that shown by the latter on the behaviour of the homogeneous ester. Now the general appearance of the $p=50$ curve indicates a minimum rotation at a temperature somewhere about 140°. The curve for $p=25$, because of its greater initial slope, probably has a minimum at a lower temperature and of lower value, whilst in the $p=10$ solution the minimum is distinct, and occurs at a temperature of about 94°. This case of quinoline is a specially complex one on account of the peculiar shape of the concentration curve (see T., 1909, **95**, 322), which itself shows a maximum, but the appearance of the graphs suggests that just as the maximum is moved by solution in nitrobenzene towards the left of the diagram, so here—the maximum having been displaced very rapidly—a minimum is coming into view, and is also being shifted from the right of the diagram towards the left. The same kind of thing is suggested by the curves for water, but, of course, only in a much less pronounced degree. It is, therefore, not improbable that on heating homogeneous ethyl tartrate to temperatures considerably above 200°, a minimum would be discovered, or, in other words, an examination of the rotation of this substance in solution in a solvent of particular type brings into view a minimum in the curve for the homogeneous compound which, perhaps, for some reason such as the high temperature at which it occurs, and consequent decomposition, could not be directly observed.

The suggestions made in the present paper seem to correlate at least much of the most systematic work which has been done on optical activity. It becomes clear why nothing in the way of comprehensive generalisation can be expected from the comparison of rotation values made at one and the same temperature for each substance, and in particular it does away with the sharp contrast which appeared to exist in certain respects between the rotation of homogeneous substances and the rotations of their solutions.

When an active substance is dissolved in a solvent, the general character of the periodic curve is, apparently, not very much altered, but the whole curve is displaced towards a lower or a higher temperature according to the nature of the solvent, the amplitude being considerably and the period perhaps slightly altered; or the solvent may have but little effect, in which case the maximum or minimum of the graph for the homogeneous compound occurs at exactly or nearly the same temperature in the solution whilst the amplitude is little changed or not at all.

### *Rotation-dispersion in Homogeneous Active Compounds.*

It is of much interest now to apply these views to a problem which, since its discovery in tartaric acid by Biot (*Mém. de l'Acad.*, 1838, **15**, 93) some seventy-five years ago, has always appeared to be one of particular difficulty, namely, that of anomalous rotation-dispersion. As a rule, the plane of polarisation of light of short wave-length is rotated most, but in certain cases this does not hold; instead, the rotation reaches a maximum value for waves of intermediate length, and the rotation-dispersion is said to be abnormal. This is, however, not a complete statement of the general case; it is, in fact, usually found, when the problem is investigated over a sufficient range of temperature, that at high temperatures the rotation-dispersion is normal, the violet rays being, say, most rotated; at intermediate temperatures it becomes abnormal, and at lower ones again it becomes normal once more, but in an opposite sense, the violet rays being least rotated.* Thus, by extrapolation from its solutions, Winther found "that homogeneous tartaric acid is lævorotatory for all colours at low temperatures; further, that the dispersion is normal at low temperatures, but becomes abnormal at about 30°, with a maximum between red and yellow. With rise of temperature this maximum moves towards the blue" (*Zeitsch. physikal. Chem.*, 1902, **41**, 187). The same peculiarity as is shown by homogeneous tartaric acid has been found by Winther in regard also to homogeneous methyl, ethyl, and *n*-propyl tartrate (*ibid.*, 177), and by Scheuer (*ibid.*, 1910, **72**, 587) for ethyl diacetyltartrate.

A considerable number of other substances have been investigated as regards this question, and in many cases the rotation-dispersion was found to be independent of the temperature and the concentration. In regard to these and his own results, Winther says (*Zeitsch. physikal. Chem.*, 1902, **41**, 195, 196): "Es ist kaum wahrscheinlich, dass diese zwei Gruppen von aktiven Körpern wirklich scharf voneinander gesondert werden können; vielmehr werden sich bei weiteren Untersuchungen gleichmässige Übergänge zwischen ihnen ergeben," and this is very probable.

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* I propose to call this negative rotation-dispersion, a large negative value of the rotation being regarded as less than a small negative value.

What is called the "rotation-dispersion coefficient" is approximately a constant for substances the dispersion of which is normal, but for such compounds as have anomalous dispersion it varies, not only in numerical value, but in sign as well. To overcome this difficulty, Winther introduced his "rational dispersion coefficient" in which the temperature of maximum rotation—the vertex of the parabolic temperature-rotation curve—played an important part (*Zeitsch. physikal. Chem.*, 1902, **41**, 207). This "rational dispersion coefficient" was found to be practically constant for methyl, ethyl, and *n*-propyl tartrate. Winther's attempt was, in fact, of just the same kind as that made by the present author a year or two later, to establish a constant relationship between the rotation values for these three esters for yellow light, and the results in both cases were of the same order (T., 1904, **85**, 765).

As has already been remarked, Winther's value for the temperature of maximum rotation was not established by experiment, but was calculated by means of a parabolic interpolation formula from experimental data obtained at temperatures up to about 60°, and his coefficient of "rational dispersion" depends expressly on the assumption "dass die maximal Temperaturen wirklich für alle Farben gleich sind" (*loc. cit.*, 209), and, considering this fact, Winther's treatment of the subject was extremely ingenious. Further, the temperature of maximum rotation which he assumed for these esters was too low, and, in addition, the value is not the same for all three.

It is, then, of much interest to inquire how the temperature of maximum rotation is related to the refrangibility of the light used. In this connexion some interesting data have been supplied by Walden (*Ber.*, 1905, **38**, 366), who has examined these three esters at various temperatures for red, green, blue, and violet light, without, however, mentioning the question of maximum rotation. These data—for observed, not specific, rotation—are represented by the curves in Figs. 7 and 8, the present author's data for yellow light being added; it will be apparent that the numbers obtained by the two different observers show very good agreement. The temperature of maximum rotation in ethyl tartrate for yellow light lies at 148°, and is marked on the curve by an *M*. It will be noticed that

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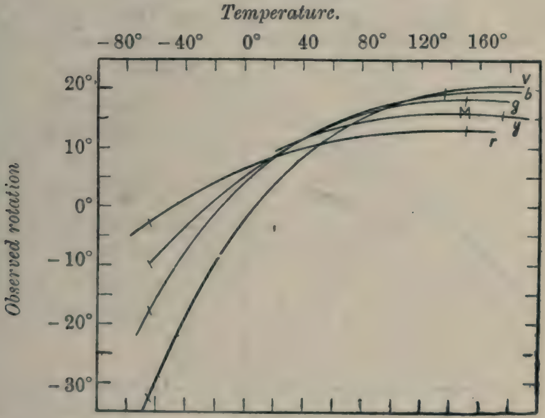
* The short cross-lines on the curves show the actual range of the observations.

Walden's data in only two cases extend beyond this.* Nevertheless, from the appearance of the curves and the actual numbers, which show that the difference between the observed values of the rotation at 100° and 135° becomes gradually greater and greater from red to violet, it may be concluded with almost complete certainty, that the maximum lies at a lower temperature than 148° for red light and at one progressively higher for green, blue, and violet.* The maximum probably moves from about 140° for red to about 180° for violet.

For propyl tartrate (Fig. 8), Walden's data fall on both sides of the maximum value for each colour of light, and here much the same thing applies. The maximum for red is 115°, that for yellow according to the determinations of the present author, is at 120°, and Walden's data give a temperature of about 125° for green and blue, and 134° for violet. The maximum thus again appears to move towards a higher temperature as the wave-length decreases.

FIG. 7.

*Ethyl tartrate. Rotation dispersion.*



Remembering what has already been suggested in the earlier part of this paper, regarding the curves for intimately related esters such as methyl and ethyl tartrate, for one colour of light, it would appear that the variation of rotation for different kinds of light in a single active ester is of a comparatively simple character. We seem to have, in these diagrams, a set of curves of similar type, varying in amplitude, which is greatest for violet and least for red, whilst, in addition, the curve for light of short wave-length is retarded a little on that of longer wave-length; so that there is a slight difference of phase. Naturally, therefore, since the period is apparently the same or nearly so, the curves cut one another successively within a certain range of temperature, just as a set of sine curves, retarded a little on each other, must have periods of intersection. If they were all in the same phase they would presumably all cut in one point, and the rotation-dispersion would be always normal, positive on one side of the point of intersection, negative on the other. Amongst these esters it is almost certainly always abnormal, but at temperatures from about 140° to 180° or higher, for ethyl tartrate, and 40° to 180° or higher, for propyl tartrate, there is a considerable separation of the curves for the different colours of light, and the abnormality is not detected. At temperatures from about +140° down to about zero or a little lower for ethyl tartrate, and from +40° down to about −40° for propyl tartrate, the curves cross each other, and the dispersion is highly abnormal. At temperatures below about 40° for methyl tartrate, zero for ethyl tartrate, and −40° for propyl tartrate, the rotation-dispersion becomes normal again, but negative (for example, ethyl tartrate at about +8°, Fig. 7).

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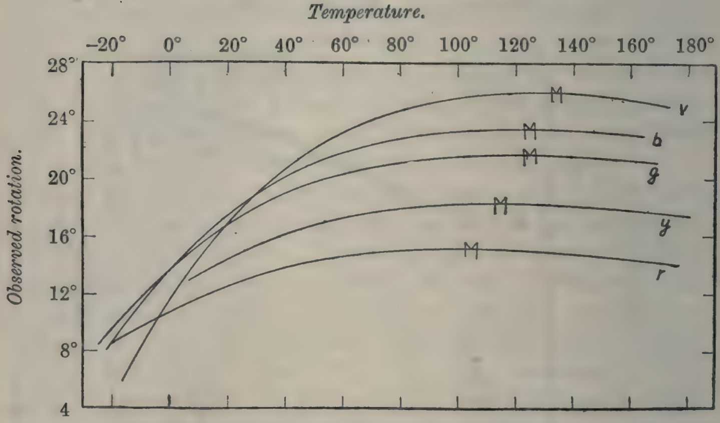
* Since the number of available data is small, the curves cannot be swept in with all the precision desirable.

Fig. 8.

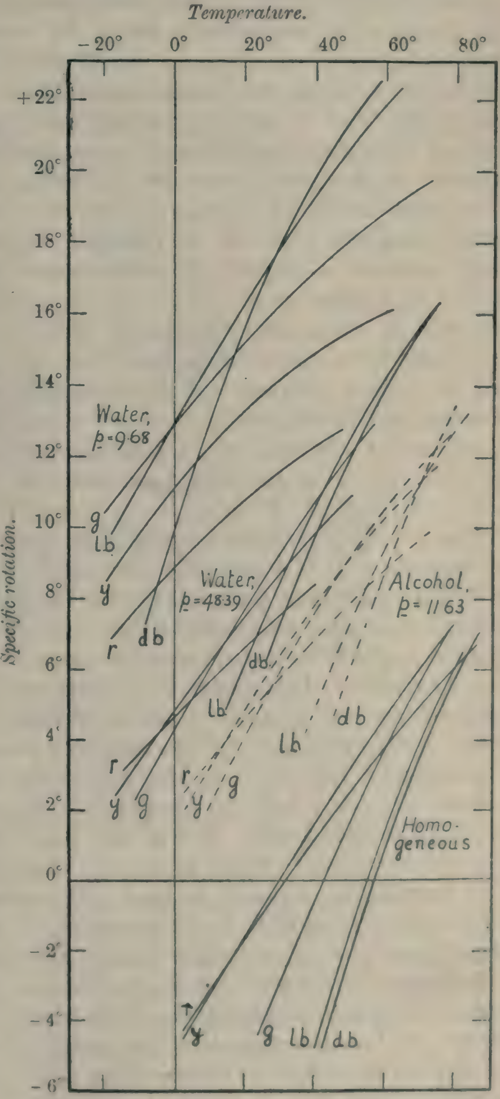
*Propyl tartrate. Rotation dispersion.*



Thus in passing from one ester to another the period of intersection of the family of curves moves towards a new rotational value and a different temperature in just the same kind of way as does the maximum rotation. Abnormal rotation-dispersion is merely the natural result of the intersection of a set of curves of different amplitude retarded a little one upon the other. Such compounds as show quite normal rotation-dispersion are probably at a temperature where, for them, a loop exists, whilst such as show abnormal dispersion are at a temperature in the neighbourhood of a node.

FIG. 9.

*Tartaric acid. Rotation dispersion.*



A point often noticed is that abnormal rotation-dispersion occurs in substances the rotation of which alters rapidly with temperature-change. The reason for this is obvious in the light of what has been said; it is between a maximum and a minimum value that the slope of the curve—the temperature-coefficient—is greatest, and it is just in this neighbourhood that the temperature-rotation curves intersect and give rise to abnormal rotation-dispersion.

### *Rotation Dispersion in Solution.*

There remains now but one other point to consider, namely, the influence of solvents on rotation-dispersion, and for this purpose very useful data have been collected by Winther. Tartaric acid may be dealt with first. By the examination of several solutions at various temperatures for light of different colours, Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 183) obtained, by extrapolation, values for the specific rotation of the homogeneous compound (*loc. cit.*, 187). These data are reproduced in Fig. 9, from which it will be seen that from temperatures of about 17° downwards the dispersion of homogeneous tartaric acid is completely normal, but negative. At 17°, or nearly, the curve for red, cuts that for yellow, light, and the rotation-dispersion begins to be abnormal, the interval of temperature before the curves are free of one another again being obviously considerable. Fig. 9 shows also the curves for a fairly concentrated solution of tartaric acid in water ($p=48{\cdot}39$), and it will be noticed that, in this case, the curve for red cuts that for yellow at a temperature of about −5°, the interval of abnormal dispersion extending up to about 70°. The curves thus begin to cut one another at a lower temperature than before, but the value of the rotation at the temperatures where they intersect is higher. In homogeneous tartaric acid, red cuts yellow at a rotation of −2·5°; in the solution this happens at a rotation of +4°. The uppermost curves of Fig. 9 represent the behaviour of a more dilute solution. The temperature at which red and yellow intersect lies so far outside the diagram that extrapolation becomes uncertain, but green and light blue, which in the concentrated solution cut at a temperature of 42° and a rotation of 11·1°, meet, in the dilute solution, at a temperature of −2° and a rotation of 12·7°.

This behaviour is thus altogether in agreement with what was to be expected. It is a fact that solution in water raises the rotation of tartaric acid, and from analogy to the behaviour of the esters of tartaric acid, the maximum, which will almost certainly be found to exist in the temperature-rotation curve for tartaric acid if means can be found to investigate the point, will move towards a lower temperature and a higher value as the result of this solution. In other words, that part of the temperature-rotation curve for the homogeneous substance in the neighbourhood of the maximum, comes, when the acid is dissolved in water, into the region of ordinary temperatures. It has just been shown, however, that in the neighbourhood of the maximum rotation, the rotation-dispersion becomes more nearly normal. Therefore, when the maximum is brought by solution into the region of ordinary temperatures, the dispersion at these temperatures, in solution, becomes normal.

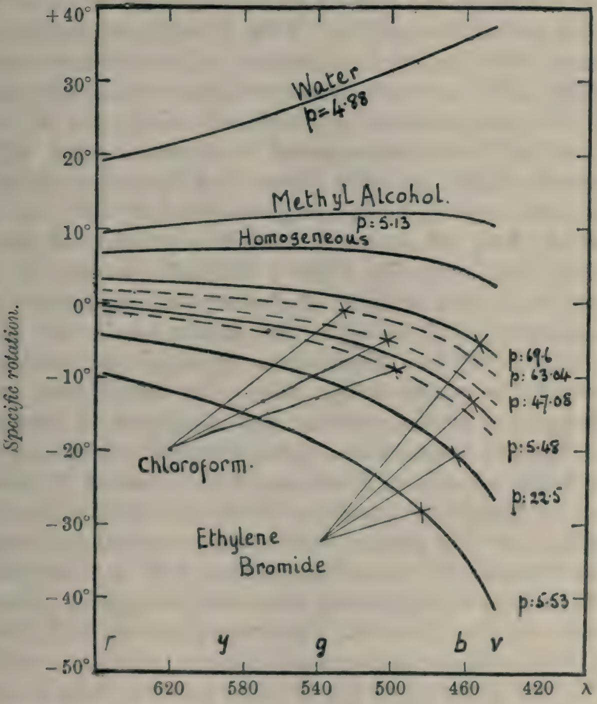
Again, whilst water raises the rotation of tartaric acid to a considerable extent, alcohol has only a slight influence in the same direction. It is therefore to be expected that the rotation-dispersion in alcohol should be much the same as in the homogeneous active substance, and this is actually found to be the case. In Fig. 9 are shown also rotation-temperature curves for tartaric acid in alcohol,

$p = 11{\cdot}63$, which may be compared with those for the homogeneous acid. In the alcoholic solution it will be noticed that at low temperatures, that is, below 10°, the dispersion is normal but negative. The curves begin to cross at about 14° when the rotation is 3·8°, and the interval of abnormal dispersion extends up to a temperature in the neighbourhood of 80°. For the homogeneous acid, as has already been said, the crossing of the curves begins at a higher temperature and a lower rotation value, and extends also to a higher temperature. The sets of curves are much alike, and are altogether consistent with the idea that solution in alcohol has the effect of shifting the temperature-rotation curves of tartaric acid towards a slightly lower temperature and a slightly higher rotation value.

FIG. 10.

*Rotation dispersion.*

*Ethyl tartrate in various solvents at 20°.*



It might, however, be objected that the maximum rotation-value for tartaric acid is not known experimentally, and therefore it will be well to examine one or two other cases. Again, valuable data are supplied by Winther, and are represented in Fig. 10 as dispersion-rotation curves for a temperature of 20°.* In dilute solution in water the rotation is high, the dispersion normal and positive; in methyl alcohol the rotation is not so much raised as in water, and the dispersion has become abnormal; chloroform gradually depresses the rotation of ethyl tartrate as the dilution increases, and we find that the abnormality has just disappeared in the most concentrated solution, but the dispersion has become negative; in ethylene bromide, which still further depresses the rotation of the ester, the dispersion may be said to have become more normal and more negative. Now it is known definitely that the maximum rotation of homogeneous ethyl tartrate moves, on dilution with water and such other solvents as raise the rotation, towards a lower temperature and a higher value, that is, into the region of ordinary temperatures, and in correspondence with this, for the reason which has been given, the dispersion in aqueous solution becomes normal in the neighbourhood of 20°. In methyl alcohol, which does not so much raise the rotation of the ethyl tartrate, the maximum is slightly shifted towards a lower temperature, and some crossing of the curves is apparent at 20°; for homogeneous ethyl tartrate the maximum is still more to the right, so that 20° is a temperature at which the most marked intersection of the curves takes place. In chloroform, however, with its depression of the rotation, the maximum is, presumably, moved out further towards the right, towards a higher temperature and a lower value, and therefore all the crossing of the curves takes place at higher temperatures than 20°, so that in Fig. 10 the dispersion, in this solvent, has become normal but negative. In ethylene bromide the same thing occurs, but in a more marked manner; the region of crossing of the curves has passed, along with the maximum rotation, to a still higher temperature, with the result that the rotation-dispersion curves become yet more negatively normal. The set of curves of Fig. 10 thus seems to form a complete whole; some property appears to progress gradually throughout the diagram irrespective of the solvent used, the curvature slowly changes from that of the lowest graph to the opposite shape in the uppermost, the rotation-dispersion changes from negative normality in ethylene bromide through abnormality to positive normality in water, and it seems, at least to the present author, that there can surely be little, if any, doubt that this is due to displacement, as the result of solvent action, of the whole set of temperature-rotation curves for the homogeneous ester, towards a lower temperature in water and a higher temperature in ethylene bromide.

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* Unfortunately, these have not been determined over a range of temperature.

The region of intersection of the family of curves for a given active compound moves to a different temperature, and assumes a new rotational value, so far as the experimental data allow of a judgment, in just the same way that the maximum rotation is displaced, by mixture with the same solvents.

It is necessary here to say a few words concerning Winther's position in regard to rotation-dispersion, in order to emphasise the very fundamental difference between it and the views developed in this paper. Winther was very clear on what may be called the empirical side of this question, but he established his "rational dispersion coefficient" on the idea, at least as a first approximation, that the temperature of maximum rotation was a constant, independent of the colour (for one and the same compound), independent also of the solvent, and independent even of substance, within the limits of a homologous series (*Zeitsch. physikal. Chem.*, 1902, **41**, 179; 1903, **45**, 334, 340 ff.; 1905, **52**, 206). "Die Mittelwerte variieren für die ganze Weinsäuregruppe, die Lösungen mitgenommen, von 137—149°" (*ibid.*, 1903, **45**, 377). All these assumptions are demonstrably incorrect. Especially does the temperature of maximum rotation vary with solution in some powerful solvent like nitrobenzene or water, passing from 175° its value in the homogeneous ester to temperatures well below zero already in only moderately dilute solutions in these solvents. From the present author's work on this subject it would seem almost certain that in a solvent like ethylene bromide, with a very strong depressing influence, the temperature of maximum rotation will move towards a higher temperature but a lower value, although the point has not been verified by direct experiment. It is therefore of peculiar interest that Winther finds by his interpolation method for propyl tartrate in ethylene bromide the following temperatures of maximum rotation at the concentrations specified (*ibid.*, 1903, **45**, 340).

| *p.* | *t.* |
|---|---|
| 74·71 | 136° |
| 45·00 | 165 |
| 15·29 | 197 |

The temperature of maximum rotation appears to move towards a higher temperature as the dilution increases, that is, as the depressing influence of the solvent increases, and this must be regarded as very strong evidence in favour of what has been developed in this and other papers in regard to the variation of the temperature of maximum rotation in different solvents and on dilution. Winther, however, for the second time in his work, deliberately rejects this information, and developed his views instead, as has been remarked, on the assumption of a constant value for the temperature of maximum rotation, so that his treatment is the very opposite of that of the present communication, in which an attempt has been made to show that it is exactly owing to the variability of the maximum—the displacement of the whole temperature-rotation curve—that most of the puzzling phenomena of optical activity are, in fact, due.*

It may be pointed out in conclusion that the object of this paper is not primarily the development of a theory. The subject-matter is indeed quite independent of any theory, except in minor points, such as in the suggestion that temperature-rotation curves are in reality periodic. A fair amount of evidence has been adduced for thinking that this is so, but if it were not the case, it still remains a fact that there is a maximum at a certain temperature in many curves; that this maximum is displaced in a certain way in passing from one member to another of a homologous or closely related series of compounds; that this maximum is found at different temperatures as the concentration is varied in a given solvent, but having a different value, and generally at different temperatures for the same concentration in different solvents; that the temperature of maximum rotation, of some compounds at least, is different for different colours of light, and this seems to be sufficient to account for the phenomena of rotation dispersion; that the region of intersection of the curves for different colours of light is displaced, as the result of solution, in just the same manner as is the maximum rotation, which appears to account for most, if not all, of the known phenomena of rotation dispersion in solution; all these statements are facts, whether the temperature-rotation curves are periodic or are parabolas, but in the former, and much more probable case, it is possible to see a relationship between the curves for substances of different type, and in the latter it is, at least, more difficult. The recognition of the displacement of a fundamental type of curve enables us to bring into one general scheme all the diverse phenomena of optical activity.

These matters also do not necessarily involve a discussion of the mechanism of the process to which the phenomena mentioned are due; it may be possible to explain all these facts in terms of the very popular, if somewhat vague—or because somewhat vague?—ideas, association, or complex formation—solvation—and it would be exceedingly interesting if some exponent of these ideas would attempt to show that it is possible to formulate a consistent scheme, based on them, and capable of withstanding even the first breath of criticism, but to the author it appears that the potentialities of the asymmetric carbon atom and of the most simple physical conception of those inter-molecular forces to which liquefaction is due,* are ample to account for all the observed behaviour.

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* It may be remarked that the expression on p. 156, by alteration of the parameters, could be made to cover the whole behaviour of active compounds, including wave-length of the light used and the influence of the solvent.

However that may be, the chief claim which the present paper makes is not to the establishment of a theory, but one much more important, namely, the recognition of the above-mentioned facts and their inter-relationship.

## EXPERIMENTAL.

### *Rotation Data.*

(Numbers marked with an asterisk are extrapolated or interpolated.)

*Ethyl Tartrate.*—The data for this ester were the same as given in T., 1908, **93**, 1852.

| $t$ ......... | 17·8° | 20·0°* | 35·3° | 60·4° | 92·9° | 124·0° | 143·0° | 160·0° | 175·0° | 200·0°* |
|---|---|---|---|---|---|---|---|---|---|---|
| $\alpha_D^{t°}$ (100 mm.) | +9·222 | 9·5 | 11·174 | 13·318 | 15·022 | 15·774 | 15·926 | 15·88 | 15·74 | 15·18 |
| $[\alpha]_D^{t°}$ .. | 7·64 | 7·87 | 9·39 | 11·45 | 13·28 | 14·35 | 14·75 | 14·95 | 14·99 | 14·87 |
| $[M]_D^{t°}$ ... | 15·74 | 16·21 | 19·34 | 23·58 | 27·35 | 29·56 | 30·38 | 30·79 | 30·88 | 30·63 |

### n-*Propyl Tartrate.*

The ester used boiled at 173—174°/17 mm.

| $t$ ...... | 16·5° | 20·0°* | 45·5° | 77·7° | 111·2° | 123·0° | 133·2° | 147·2° | 161·0° | 173·0° |
|---|---|---|---|---|---|---|---|---|---|---|
| $d$ ...... | 1·1407 | 1·1375 | 1·1127 | 1·0819 | 1·0487 | 1·0372 | 1·0272 | 1·0128 | 0·9990 | 0·987 |
| $[\alpha]_D^{t°}$ (100 mm.) | 13·94° | 14·17° | 16·16° | 17·83° | 18·29° | 18·27° | 18·20° | 18·05° | 17·75° | 17·47 |
| $[\alpha]^{t°}$ ... | 12·22 | 12·54 | 14·52 | 16·48 | 17·44 | 17·62 | 17·72 | 17·82 | 17·77 | 17·70 |
| $[M]_D^{t}$ ... | 28·60 | 29·34 | 33·98 | 38·56 | 40·81 | 41·23 | 41·47 | 41·70 | 41·58 | 41·42 |

Densities determined:

| $t$............ | 15·26° | 39·9 | 75·8 | 132·5 | 167·0 |
|---|---|---|---|---|---|
| $d$ ......... | 1·1420 | 1·1185 | 1·0836 | 1·0279 | 0·9927 |

### sec.-*Propyl Tartrate.*

The ester was prepared by Fischer and Speier's method. It boiled at 157—158°/16 mm.

| $t$ ...... | 15·3° | 20·0°* | 49·7° | 73·0° | 118·0° | 136·0° | 144·5° | 155·0° | 173·0° |
|---|---|---|---|---|---|---|---|---|---|
| $d$ ...... | 1·1145 | 1·1100 | 1·0810 | 1·0580 | 1·0124 | 0·9934 | 0·9845 | 0·9734 | 0·9535 |
| $\alpha_D^{t°}$ (100 mm.) | 22·9° | 23·36° | 24·5° | 25·04° | 25·01° | 24·66° | 24·405° | 24·11° | 23·48° |
| $[\alpha]_D^{t°}$ ... | 20·55 | 20·90 | 22·66 | 23·67 | 24·69 | 24·82 | 24·79 | 24·77 | 24·63 |
| $[M]_D^{t°}$ ... | 47·97 | 48·91 | 53·02 | 53·38 | 57·77 | 58·07 | 58·00 | 57·96 | 57·63 |

---

* Which, after all, may embrace that departure, in moderately concentrated solutions, from the laws which are only valid for infinitely dilute solutions, and which is often regarded, without any proper reason, as an indication of association.

Densities determined:

| | | | | |
|---|---|---|---|---|
| $t^{\circ}$ ......... | 13·66° | 40·6° | 79·75° | 15·0° |
| $d$ ......... | 1·1162 | 1·0899 | 1·0513 | 0·9789 |

### *Allyl Tartrate.*

The ester was prepared by boiling tartaric acid with allyl alcohol for some hours, and distilling off the excess of alcohol as far as possible. Fresh alcohol was then added, the mixture again boiled for several hours, the alcohol distilled off, and the ester fractionated. It boiled at 191°/20 mm., 182°/15 mm., and 171°/10 mm.

For hydrolysis 2·0894 grams required 13·8 c.c. of 1·337*N*-potassium hydroxide. Theory demands 13·6 c.c.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $t$ ...... | 15·6° | 20·0°* | 33·2° | 71·5° | 106·6° | 18·4° | 131·6° | 148·2° | 168·0° |
| $d$ ...... | 1·1988 | 1·1941 | 1·1813 | 1·1435 | 1·1097 | 1·1956 | 1·0842 | 1·0672 | 1·0475 |
| $\alpha_{D}^{t^{\circ}}$ (100 mm.) | 18·314° | 18·57° | 19·168° | 20·522° | 20·706° | 18·32° | 20·40° | 20·024° | 19·31° |
| $[\alpha]_{D}^{t^{\circ}}$ ... | 15 28 | 15·52 | 16·23 | 17·95 | 18·66 | 15·32 | 18·82 | 18·76 | 18·44 |
| $[M]_{D}^{t}$ ... | 35·15 | 35·70 | 37·32 | 41·28 | 42·92 | 35·24 | 43·29 | 43·15 | 42·41 |

Densities determined:

| | | | | | |
|---|---|---|---|---|---|
| $t$ ...... | 26·6° | 38·5° | 48·75° | 80·0° | 148·5° |
| $d$ ...... | 1·1874 | 1·1757 | 1·1654 | 1·1350 | 1·0669 |

### iso*Butyl Tartrate.*

Two different specimens of *iso*butyl tartrate were used, one prepared from the dextro-acid and the other from the lævo-acid. The rotation values agree almost exactly. The boiling point of both was 185°/21 mm., and the melting point 73—74°.

### iso*Butyl* d-*Tartrate.*

| | | | | |
|---|---|---|---|---|
| $t$ .................. | 20·0°* | 97·5° | 80·6° | 69·1° |
| $d$ ................ .. | — | 1·0106 | 1·0257 | 1·0362 |
| $\alpha_{D}^{t^{\circ}}$ (100 mm.) ... | +19·8° | +20·66° | +20·56° | +20·55° |
| $[\alpha]^{t^{\circ}}$ ................ | 17·75 | +20·44 | +20·03 | +19·83 |
| $[M]_{D}^{t}$ ... .......... | 46·5 | +53·55 | +52·47 | +51·96 |

Densities determined:

| | | | |
|---|---|---|---|
| $t$ ............... | 75·2° | 86·2° | 97·7° |
| $d$ ............... | 1·0309 | 1·0206 | 1·0105 |

### iso*Butyl* l-*Tartrate.*

| | | | | |
|---|---|---|---|---|
| $t$ .................. | 78·6° | 97·5° | 121·3° | 148·7° |
| $d$ ............... | 1·0295 | 1·0115 | 0·9887 | 0·9676 |
| $\alpha_{D}^{t^{\circ}}$ (100 mm.)... | −20·60° | −20·64° | −20·34° | −19·64° |
| $[\alpha]^{t^{\circ}}$ ............ | −20·01 | −20·40 | −20·57 | −20·29 |
| $[M]_{D}^{t^{\circ}}$ .. ......... | −52·43 | −53·45 | −53·9 | −53·17 |

Densities determined:

| | | | | |
|---|---|---|---|---|
| $t$ | 98·2° | 108·6° | 130·2° | 146·0° |
| $d$ | 1·0107 | 1·0075 | 0·9809 | 0·9649 |

### *Dï*iso*amyl Tartrate.*

This ester was prepared, by the hydrogen chloride saturation method, from a so-called *iso*amyl alcohol supplied by Kahlbaum, having a rotation of $-2·262°$ in a 2-dcm. tube at 15·5°. The ester boiled at 195°/16 mm.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $t$ | 15·6° | 20·0°* | 40·7° | 92·0° | 131·2° | 157·0° | 175·0° |
| $d$ | 1·0669 | 1·0585 | 1·0400 | 0·9943 | 0·9596 | 0·9365 | 0·9205 |
| $\alpha_D^{t°}$ (100 mm.) | 12·077° | 12·45° | 13·995° | 15·992° | 16·047° | 15·722° | 15·368° |
| $[\alpha]_D^{t°}$ | 11·32 | 11·73 | 13·46 | 16·01 | 16·72 | 16·79 | 16·69 |
| $[M]_D^{t°}$ | 32·83 | 34·02 | 39·04 | 46·43 | 48·49 | 48·69 | 48·40 |

Densities determined:

| | | | | |
|---|---|---|---|---|
| $t$ | 14·75° | 43·3° | 77·9° | 167·0° |
| $d$ | 1·0631 | 1·0379 | 1·0080 | 0·9278 |

### *Di*sec.*-octyl Tartrate.*

This ester was prepared by heating a mixture of tartaric acid and *sec.*-octyl alcohol in a flask on the water-bath and passing dry hydrogen chloride through the liquid for about four days. The excess of octyl alcohol was then distilled off, fresh alcohol added, and the current of hydrogen chloride again passed into the liquid for about five days more. The octyl alcohol was then removed by distillation, the residue shaken with sodium carbonate solution, dissolved in ether, this solution dried with calcium chloride, the ether removed, and the ester distilled under diminished pressure. The octyl tartrate boiled at 239°/15 mm. and at 194°/3 mm.

| | | | | | | |
|---|---|---|---|---|---|---|
| $t$ | 16·4° | 20·0°* | 41·0° | 74·4° | 107·5° | 133·0° |
| $d$ | 1·0055 | 0·9992 | 0·9825 | 0·9557 | 0·9291 | 0·9087 |
| $\alpha_D^{t°}$ (100 mm.) | 10·256° | 10·4° | 11·18° | 11·98° | 12·37° | 12·34° |
| $[\alpha]^{t°}$ | 10·25 | 10·45 | 11·38 | 12·54 | 13·31 | 13·58 |
| $[M]_D^{t°}$ | 38·33 | 39·09 | 42·56 | 46·89 | 49·78 | 50·77 |

| | | | | | |
|---|---|---|---|---|---|
| $t$ | 159·0° | 173·0° | 179·0° | 131·5° | 200·0° * |
| $d$ | 0·8880 | 0·8766 | 0·8719 | 0·9099 | 0·8549 |
| $\alpha_D^{t°}$ (100 mm.) | 12·21° | 11·98° | 11·89° | 12·38° | 11·35° |
| $[\alpha]_D^{t°}$ | 13·75 | 13·67 | 13·64 | 13·60 | 13·28 |
| $[M]_D^{t°}$ | 51·41 | 51·11 | 51·00 | 50·88 | 49·65 |

Densities determined:

| | | | | | |
|---|---|---|---|---|---|
| $t$ | 18·6° | 36·45° | 53·1° | 70·65° | 100·1° |
| $d$ | 1·0006 | 0·9861 | 0·9727 | 0·9587 | 0·9353 |

*sec.*-Octyl tartrate was first prepared by McCrae (T., 1902, **81**, 1221; see also T., 1901, **79**, 1103) by a method suggested by Patterson and Dickinson (T., 1901, **79**, 280). McCrae gave as the molecular rotation of the compound $[M]_D^{20}$ + 22·55°, and states that on account of the insolubility of tartaric acid in octyl alcohol, the hydrogen chloride method cannot be used in this case. The rotation of the ester examined in this investigation was very considerably higher than that quoted by McCrae, and in order to ascertain which observation was correct a new preparation was on the point of being started when a paper appeared by Pickard and Kenyon (T., 1911, **99**, 67) containing a description of di-β-octyl *d*-tartrate. These authors prepared their ester by Patterson and Dickinson's method from dimethyl and diethyl tartrate. They give the boiling points as 202—210°/6 mm., and the rotation as $[M]_D^{17}$ + 41·1°, which agrees fairly well with the above estimation, but not at all with that recorded by McCrae, whose preparation was therefore contaminated with a considerable proportion of ethyl octyl tartrate. The discrepancy between the rotation of Pickard and Kenyon and that of the present author may perhaps be ascribed partly, at least, to a slight difference in the rotation of the octyl alcohol used.

### *Dibenzyl Tartrate.**

Freundler (*Ann. Chim. Phys.*, 1894, [vii], **3**, 448) records two unsuccessful attempts to prepare this compound, the first by passing hydrogen chloride through a mixture of tartaric acid and benzyl alcohol, and the other by heating silver tartrate with benzyl chloride. He remarks that benzyl tartrate decomposes on distillation. Nevertheless, benzyl tartrate is quite easily obtained by heating tartaric acid and benzyl alcohol for some hours in a distilling flask fitted to a condenser. In quite a short time all the acid passes into solution, and water begins to separate. If the liquid be kept gently boiling, water and a little benzyl alcohol pass over. The mixture may then be distilled under diminished pressure until all the alcohol has passed over, or the latter may be removed by a current of steam. The former method is the simpler, since the residue can be distilled immediately without further treatment, but the distillation must be carried out at a low pressure of about 4 mm., when the substance boils at about 250—270°. Since the distillation can only be done on rather small quantities, it is difficult to get an accurate determination of this constant. The compound melts somewhat indefinitely in the neighbourhood of 50°. It forms a solid rather resembling fat, consisting of very fine hair-like crystals. It can be crystallised from ether, ethyl acetate, or benzene, but the crystals formed are so fine that it seems impossible to separate them from the mother liquor, either by the aid of the pump or on porous plate; it separates from benzene as a remarkably close imitation of a jelly.

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* Medinger (*J. pr. Chem.*, 1912, [ii], **86**, 345) describes the preparation of benzyl tartrate (a viscid, yellow oil) by heating benzyl alcohol, tartaric acid, and potassium hydrogen sulphate.

For hydrolysis, 1·7558 grams of the distilled ester required 23·14 c.c. of 0·4625*N*-potassium hydroxide. Theory demands 23·01 c.c.

*Rotation Data.*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $t$ ......... | 36·0° | 21·2° | 51·5° | 71·5° | 93·0° | 116·0° | 138·0° | 170·8° | 15·0° |
| $d$ ......... | 1·2360 | 1·2493 | 1·2220 | 1·2038 | 1·1845 | 1·1639 | 1·1443 | 1·1089 | 1·2550 |
| $\alpha_D^{t°}$ (100 mm.) | 25·05° | 24·365° | 25·535° | 26·0° | 26·005° | 25·61° | 25·045° | 23·88° | 24·17° |
| $[\alpha]_D^{t°}$ ... | 20·27 | 19·50 | 20·90 | 21·6 | 21·95 | 22·0 | 21·89 | 21·49 | 19·26 |
| $[M]_D^{t°}$ ... | 66·89 | 64·36 | 68·96 | 71·28 | 72·45 | 72·62 | 72·23 | 70·92 | 63·56 |

Densities determined:

| | | | | |
|---|---|---|---|---|
| $t$ .............. | 72·2° | 96·8° | 152° | 167° |
| $d$ .............. | 1·2036 | 1·1808 | 1·1322 | 1·1184 |

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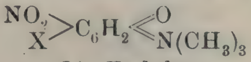
# XXII.—*Quinone-ammonium Derivatives. Part II. Nitro-haloid, Dihaloid and Azo-compounds.*

By Raphael Meldola and William Francis Hollely.

The products of the extreme methylation of the picramic acids by methyl sulphate in the presence of alkali hydroxide have been shown in a former paper (T., 1912, **101**, 912) to be dinitro-derivatives of trimethylammonium-benzoquinone. These compounds are of an ochreous colour in the anhydrous "quinonoid" form, that from *iso*picramic acid being red in the hydrated form, for which a quinole structure has been suggested (*loc. cit.*, p. 918). The relationship of these compounds to the iminazolium compounds and iminazolones described in a series of previous communications to the Society has also been indicated (*loc. cit.*, p. 921). The research has accordingly been extended with the object, in the first place, of obtaining further evidence with respect to the influence of the substituents on the colour of the compound, and in the next place, with the object of preparing, if possible, quinone-ammonium derivatives containing an asymmetric nitrogen atom for comparison with the iminazolium compounds and iminazolones referred to. The first line of investigation has been successfully followed up, and the results are made known in the present paper. The second series of experiments have presented unforeseen practical difficulties, owing to the great tendency on the part of the amino-group in the aminophenols and their derivatives to undergo complete alkylation instead of partial substitution. This branch of the research is being continued.

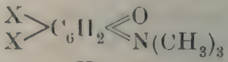
The preparation of the halogen derivatives of the quinone-ammonium compounds has been much facilitated by the discovery that the nitro-groups in the nitro-derivatives are quite readily brought under the control of reducing agents with partial or complete reduction. The complete or partial replacement of these groups by halogens by the diazo-reaction has thus been made possible, and compounds of the types:



$$\genfrac{}{}{0pt}{}{NO_2}{X}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{O}{N(CH_3)_3}$$

(I.) X = halogen.

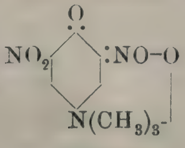
and



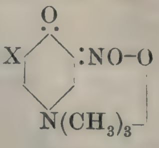
$$\genfrac{}{}{0pt}{}{X}{X}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{O}{N(CH_3)_3}$$

(II.)

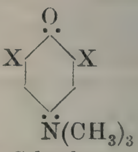
have been prepared. The dependence of the colour of these compounds upon the presence of the nitro-group is conclusively established by the fact that compounds of type I are ochreous, and those of class II colourless. The constitution of these haloid derivatives, so far as concerns the positions of the substituents, is in all cases established by the constitution of the parent compounds. The complete disappearance of colour when both nitro-groups are replaced by halogens may, so far as the chemical evidence goes, be fairly interpreted by assigning a different constitution to the nitro-derivatives. This possibility, which was indicated in our last paper, receives further support from the present extension of the research. Thus, taking the series from *iso*picramic acid, which has been the more completely investigated, it will be seen that no ortho-quinonoid structure is possible in the case of the dihaloid derivatives. The association of colour as a property with the possibility of assuming meta cross-linking thus appears to be a justifiable hypothesis, it being understood that the term "quinonoid" covers both ketonoid and cross-linked forms:



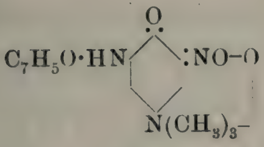
Ochreous.



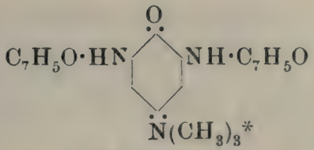
Ochreous.



Colourless.

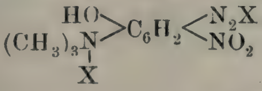


Ochreous.

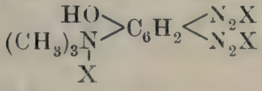


Colourless.

Not the least interesting character of the amino- and diamino-derivatives of the quinone-ammonium compounds is the readiness with which they can be diazotised. The di- or bisdi-azonium salts, being formed in acid solutions, are no doubt of the types:



$$\begin{array}{l}HO\\(CH_3)_3\underset{\substack{|\\X}}{N}\end{array}\!>C_6H_2<\!\begin{array}{l}N_2X\\NO_2\end{array}$$

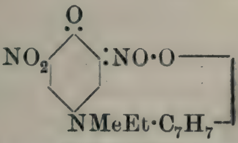


$$\begin{array}{l}HO\\(CH_3)_3\underset{\substack{|\\X}}{N}\end{array}\!>C_6H_2<\!\begin{array}{l}N_2X\\N_2X\end{array}$$

X = acid radicle.

Direct evidence of the existence of compounds of these types is furnished by the fact that the actual salts of the corresponding azo- and bisazo-compounds have been isolated. These azo-derivatives belong to a new type, and as they promise to be of exceptional interest, their detailed study is being continued.

We may take the present opportunity of placing preliminarily upon record the successful isolation of the first compound of the present series containing an asymmetric nitrogen atom, namely, the quinone-ammonium derivative from *iso*picramic acid containing the radicles methyl, ethyl, and benzyl attached to the same nitrogen atom:



(or alternative formula).

This compound should be resolvable into optical isomerides, but its intractable character has hitherto offered insuperable obstacles to its investigation, and much experimental work will be necessary before we can hope to accomplish a successful resolution.

## EXPERIMENTAL.

The partial reduction of 2 : 6-dinitro-4-trimethylammonium-1-benzoquinone (T., 1912, **101**, 927) † is readily effected by gently boiling the substance with dilute ammonia and ammonium sulphide until it passes completely into solution and no longer crystallises out on cooling. The solution, on acidification with hydrochloric acid, and after removal of sulphur by filtration, contains the very soluble chloride of the nitroamino-derivative. Neither the salts nor the free base could be isolated on account of their extreme solubility in water, so the solution was made alkaline by sodium hydroxide and agitated with benzoyl chloride, as in the Schotten-Baumann process. The resinous mass thus formed was collected, washed with water, and purified by solution in hydrochloric acid and reprecipitation by ammonia. After two crystallisations from hot water, the compound had a constant decomposing point of 282—283°, showing signs of darkening from about 265°. It crystallises in long, slender, golden needles:

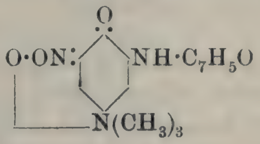
---

* Described in last paper, *loc. cit.*, p. 929.

† The third alternative formula given in the above paper (p. 927) is erroneously printed. The para-*N*-atom should be singly and not doubly linked to the benzene nucleus.

0·1033 gave 0·2299 $CO_2$ and 0·0508 $H_2O$. C=60·70; H=5·46.
0·1012 ,, 11·9 c.c. $N_2$ (moist) at 18·5° and 751 mm. N=13·39.
$C_{16}H_{17}O_4N_3$ requires C=60·92; H=5·44; N=13·33 per cent.

From its mode of formation the compound is 6-*nitro*-2-*benzoylamino*-4-*trimethylammonium*-1-*benzoquinone*:



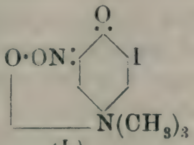
(or alternative linking).

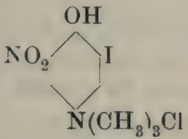
## *Nitro-haloid Derivatives.*

The reducibility of one of the nitro-groups having been proved to be possible by the isolation of the above compound, experiments were undertaken with the object of introducing a halogen atom in place of the amino-group. The diazotised nitroamino-compound was found to be readily amenable to treatment by the Sandmeyer process, but in the case of the chloro- and bromo-derivatives the products were too soluble in water to allow of their separation from the inorganic salts contained in the solution. The iodonitro derivative was prepared by reducing the dinitroquinone-ammonium compound with ammonium sulphide as described above, and diazotising the acidified solution with sodium nitrite. On mixing the solution containing the diazonium salt with a concentrated solution of potassium iodide and completing the reaction by the application of heat in the usual way, the iodonitro-compound separates on cooling as a dense, microcrystalline deposit. The latter was collected, washed with water, then with dilute sodium hydroxide to remove free iodine, and then again with water. After crystallisation from hot water, in which the compound is fairly soluble, ochreous needles were obtained, which had no definite melting point, but which commenced charring about 200° and remained unchanged up to 300°. The air-dried substance undergoes no loss on heating, and proved on analysis to be the anhydride:

0·1722 gave 12·75 c.c. $N_2$ (moist) at 18° and 766·8 mm. N = 8·63.
0·2564 „ 0·1849 AgI. I = 38·95.
$C_9H_{11}O_3N_2I$ requires N = 8·69; I = 39·42 per cent.

The compound is accordingly 2-*iodo*-6-*nitro*-4-*trimethylammonium*-1-*benzoquinone* (I):


(I.)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The presence of two nitro-groups in the original dinitroquinone-ammonium compound so far enfeebles the basicity of the molecule that no stable salts could be isolated (T., 1912, **101**, 928). The substitution of iodine for one of the nitro-groups restores the basic character of the compound to a sufficient extent to enable it to form stable salts, the transition from the coloured form to a colourless salt (No. II above) on the breaking down of the quinonoid structure being most striking. The *chloride* was prepared by dissolving the iodonitro-compound in hot dilute hydrochloric acid and allowing the solution to cool, when the salt separates in small, silvery scales, showing prismatic colours in the solution:

0·1986 gave 13·1 c.c. $N_2$ (moist) at 19° and 771·3 mm. N = 7·70.
0·3236, decomposed in aqueous solution with silver nitrate, gave 0·1324 AgCl. Cl = 10·11.
$C_9H_{12}O_3N_2ClI$ requires N = 7·82; Cl = 9·89 per cent.

An attempt to prepare the nitrate led to the discovery that the iodine atom in the iodonitro-compound is readily displaceable by the nitro-group. The solution obtained by decomposing the chloride with silver nitrate and filtering off the silver chloride gave, on evaporation, a substance which crystallised in long, yellow needles, which on analysis were found to contain 11·96 per cent. of nitrogen, the nitrate requiring 10·91 per cent. The colour of this salt and the high percentage of nitrogen pointed to the conclusion that the free nitric acid was re-nitrating the compound with the liberation of iodine. This conclusion was verified by several experiments, the salt obtained by dissolving the iodonitro-compound in dilute nitric acid, and which consists of colourless needles, even after drying in the air, was found to contain 12·2 per cent. of nitrogen. The iodonitro-compound dissolves also in nitric acid (D 1·42), with the immediate liberation of iodine and the formation of the original dinitroquinone-ammonium compound.

### 2-*Bromo*-6-*nitro*-4-*trimethylammonium*-1-*benzoquinone*.

As already stated in the introductory portion of this paper, the solubility of the bromonitro-derivative in water has prevented its preparation through the nitroamino-compound and the diazo-reaction. We have, however, succeeded in preparing a small quantity of the substance by another method, which, although leaving much to be desired in the way of yield, appears to be worthy of further elaboration. This method consists in methylating bromonitro-*p*-aminophenol prepared as described below.

Monobenzoyl-*p*-aminophenol * is dissolved in a small quantity of hot glacial acetic acid, and the solution mixed with an acetic acid solution of bromine containing one molecular proportion of the latter. The solution is allowed to remain for some hours at the ordinary temperature and then heated in order to complete the reaction and to expel hydrogen bromide. The crude substance is precipitated in a granular state by pouring the hot acetic acid solution into cold water with brisk agitation. Purification is effected by crystallisation from dilute alcohol with animal charcoal, the pure compound crystallising in white needles, melting at 184—185°:

0·0914 gave 3·9 c.c. $N_2$ (moist) at 19° and 769·4 mm. N = 4·96.

$C_{13}H_{10}O_2NBr$ requires N = 4·79 per cent.

From its mode of formation the compound is no doubt the benzoyl derivative of the 2-bromo-4-aminophenol described by Hölz (*J. pr. Chem.*, 1885, [ii], **32**, 65). Confirmation of this is furnished by the behaviour of the compound on nitration, when it yields a bromonitro-derivative analogous to *iso*picramic acid in all its properties. In order to nitrate the bromo-compound, the latter is suspended in well-cooled glacial acetic acid and a mixture of fuming nitric acid (D 1·5) with an equal volume of acetic acid, this mixture being also well cooled, is gradually added with constant stirring. In a short time the bromo-compound is converted into the nitro-derivative, and the contents of the beaker solidify to a crystalline pulp. At this stage the addition of nitric acid must at once be stopped, as the product dissolves in excess of acid with complete decomposition. On completion of the nitration the pulpy mass is immediately stirred into water containing ice, collected, washed, and dissolved in hot dilute ammonia, from which solution the ammonium salt crystallises out, on cooling, in orange needles, similar in appearance to the ammonium salt of benzoyl-*iso*picramic acid. The pure compound, obtained from the ammonium salt by decomposing the latter with dilute hydrochloric acid, is but sparingly soluble in boiling alcohol. It crystallises from this solvent in brilliant, golden-yellow scales, melting at 257°:

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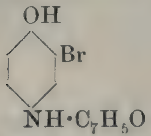
* The preparation of this substance is described in a paper communicated to *The Chemical World* for October, 1912; Vol. I., p. 327.

0·2481 gave 16·97 c.c. $N_2$ (moist) at 13° and 768·9 mm. N=8·18.
0·2234 ,, 0·1255 AgBr. Br=23·90.
$C_{13}H_9O_4N_2Br$ requires N=8·31; Br=23·72 per cent.

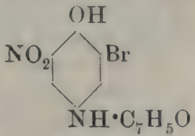
The hydrolysis of the above compound was effected by heating with excess of concentrated sulphuric acid until a drop of the solution, on dilution with water, on a watch-glass gave no indication of the presence of undecomposed substance. A somewhat high temperature is required for the hydrolysis, and the sulphuric acid solution must be kept for some time just at the point when it shows indications of fuming, as in the corresponding process for the hydrolysis of benzoyl*iso*picramic acid. There is much loss at this stage, owing to secondary decomposition, and we have not been enabled to obtain better results by using diluted acid or with the acetyl derivative instead of the benzoyl derivative. Should this bromonitro-*p*-aminophenol prove to be of special value in the future extension of the research, as seems likely to be the case, we hope to be able to revise and improve the process for preparing it. When the hydrolysis was complete, the sulphuric acid solution was allowed to cool, poured into cold water, filtered to remove benzoic acid and resinous impurity, and neutralised with ammonia. After remaining for some hours the crude product which separated was collected, washed with water, and purified by repeated solution in cold hydrochloric acid, filtration, and reprecipitation by neutralisation with ammonia until it dissolved in hydrochloric acid without leaving any residue. The *bromonitro*-p-*aminophenol* thus obtained crystallises from dilute alcohol in deep reddish-brown scales or needles, melting at 149°. It is both phenolic and basic, forming colourless salts with acids, and dissolving in sodium hydroxide solution with an orange colour. The presence of bromine was proved qualitatively:

0·1423 gave 14·3 c.c. $N_2$ (moist) at 16·5° and 769·5 mm. N=11·83.
$C_6H_5O_3N_2Br$ requires N=12·02 per cent.

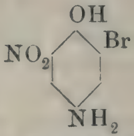
The formulæ of these compounds, which do not appear to have been described before, are given below:



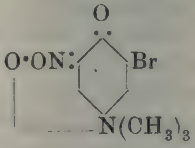
M. p. 184—185°.
(I.)



M. p. 257°.
(II.)



M. p. 149°.
(III.)



(IV.)

2-*Bromo*-6-*nitro*-4-*trimethylammonium*-1-*benzoquinone* (No. IV above) was prepared by methylating the bromonitrophenol with methyl sulphate and sodium hydroxide solution in the usual way. The product is more soluble in water than the corresponding dinitro-compound, so that the methylation must be carried out in a minimum quantity of water. Purification was effected by dissolving the compound in hydrochloric acid, filtering, and adding ammonia in excess to the acid solution. As the solution cools, the substance crystallises in large, orange scales, which, when dried in the air, consist of the hydrated form with an additional molecule of water. The decomposing point is 220—225°. The compound loses all its water at 100°, and the colour changes from orange to ochreous yellow:

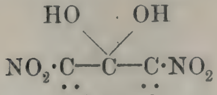
0·1193, dried at 100°, gave 10·7 c.c. $N_2$ (moist) at 15° and 736·5 mm. N=10·17.

$C_9H_{11}O_3N_2Br$ requires N=10·18 per cent.

0·3363, air-dried, lost 0·0387 at 100°=11·51 $H_2O$.

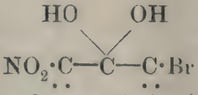
$C_9H_{11}O_3N_2Br,2H_2O-2H_2O$ requires a loss=11·58 per cent.

The fact that the bromonitro-compound forms a coloured hydrate like the dinitro-compound, whilst the iodonitro-compound forms no hydrate, is quite in harmony with the quinole structure for the hydrated form (T., 1912, **101**, 918), since the existence of this type of structure is dependent upon the central carbon atom being between carbon atoms attached to strongly acid radicals. Thus, the nitro-group and bromine atom are sufficiently acid, whilst the iodine atom is not:



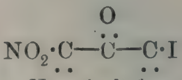
$\mathrm{NO_2\cdot\underset{\cdot\cdot}{C}-\overset{HO\ \ \ OH}{C}-\underset{\cdot\cdot}{C}\cdot NO_2}$

Red quinole.



$\mathrm{NO_2\cdot\underset{\cdot\cdot}{C}-\overset{HO\ \ \ OH}{C}-\underset{\cdot\cdot}{C}\cdot Br}$

Orange quinole.



$\mathrm{NO_2\cdot\underset{\cdot\cdot}{C}-\overset{O}{\overset{\cdot\cdot}{C}}-\underset{\cdot\cdot}{C}\cdot I}$

No quinole.*

From these results it may be predicted that the chloronitro-compound would form a hydrate redder in colour than the bromonitro-compound. We hope to be able to submit this prediction to experimental proof on some future occasion, although, as already stated, the isolation of the chloronitroquinone-ammonium derivative has hitherto been found impracticable. The methylation of 2-chloro-6-nitro-4-aminophenol (D.R.-P. 147060; A., 1904, i, 311) should yield the required compound.

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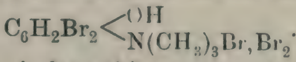
* The nitro-groups in the above formulæ are represented as normal and not as "*aci*" for the sake of simplicity.

### *Dihaloid Derivatives.*

The synthesis of the dinitroquinone-ammonium derivatives by the nitration of the unsubstituted parent compounds (T., 1912, **101**, 915) indicated the possibility of directly introducing halogen atoms into the nucleus by a similar process. Some such method was rendered necessary by the fact, already mentioned, that the haloid (chloro- and bromo-) derivatives were too soluble in water to enable them to be conveniently separated from the inorganic salts present in the solution when using the ordinary (Sandmeyer) method of decomposing the diazonium salts. Gattermann's modification of the diazo-reaction would most probably enable these compounds to be prepared by this method, and we propose making experiments in this direction. In the meantime we have succeeded in preparing the dibromo-derivative by direct bromination, as described below.

### 2 : 6-*Dibromo*-4-*trimethylammonium*-1-*benzoquinone.*

*p*-Aminophenol was methylated by methyl iodide and potassium hydroxide in methyl-alcoholic solution, according to the method of Griess, and the iodide, after purification by crystallisation from water, converted into the nitrate by decomposition with silver nitrate. The aqueous solution of the nitrate was used for bromination. On adding an acetic acid solution of bromine to the solution of the nitrate, a dense, crystalline, ochreous precipitate is formed, and the bromine solution is added with constant stirring as long as a turbidity appears on mixing the solutions. The ochreous precipitate consists no doubt of the perbromide of the dibromo-derivative,  $C_6H_2Br_2{<}\begin{smallmatrix}OH\\N(CH_3)_3Br,Br_2\end{smallmatrix}$. It was not found possible, however, to isolate this compound, as it is unstable and decomposes with the evolution of bromine on exposure to the air. The washed product was therefore decomposed by aqueous ammonia, in which it dissolved with copious evolution of nitrogen, and the solution, on acidification with hydrochloric acid, slowly deposited dense, colourless prisms of the chloride of the ammonium compound. Numerous analyses of various preparations at this stage proved that the salt had the required formula, but it was difficult to obtain concordant results owing to the retention of two molecules of water of crystallisation and the tendency to partial efflorescence on drying. A purer salt was afterwards prepared directly from the base, the latter being obtained from the crude chloride by dissolving the salt in water, agitating the hot solution with excess of moist silver oxide, filtering, and evaporating the solution to the crystallising point. The base separated out on cooling in colourless, fern-like leaflets, which retained water at the atmospheric temperature, but which lost water and fell to an opaque, white powder on drying at 110—115°. The compound decomposes at about 207°. The loss of water at 100° was not quite complete, but indicated the retention of three molecules (loss = 13·97 instead of 14·88 per cent.). The substance, when dried at 110—115°, gave the following results:

0·1836 gave 7·35 c.c. $N_2$ (moist) at 21° and 764·6 mm. N = 4·58.
0·2473 ,, 0·3020 AgBr (method of Carius). Br = 51·96.
$C_9H_{11}ONBr_2$ requires N = 4·53; Br = 51·75 per cent.

A specimen of the chloride, prepared from the base by dissolving the latter in hot water, adding hydrochloric acid and allowing to crystallise, consisted of long, transparent, colourless prisms, which began to char at about 200° and decomposed at 220—224°:

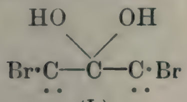
0·5824 (air-dried) lost 0·0556 at 100°, the crystals becoming opaque without losing their form, and having a decomposing point of 227—228°: The loss, $H_2O$ = 9·54 per cent.
0·2213 (oven-dried) gave 7·9 c.c. $N_2$ (moist) at 17° and 761·6 mm. N = 4·15.
0·2696 (oven-dried), decomposed in aqueous solution with silver nitrate, gave 0·1137 AgCl. Cl = 10·42.
$C_9H_{12}ONClBr_2$ requires N = 4·05; Cl = 10·26 per cent.
The loss, $C_9H_{12}ONClBr_2,2H_2O - 2H_2O$ = 9·44 per cent.

The *picrate* was prepared by mixing a hot aqueous solution of the base with the calculated quantity of picric acid dissolved in hot water. The salt crystallises out on cooling in transparent, yellow scales, decomposing from 198° to 208°. It is but sparingly soluble in alcohol, and crystallises from this solvent in rosettes of yellow, stumpy prisms or serrated leaflets, both forms melting and decomposing at 206—207°:

0·1032 gave 9·3 c.c. $N_2$ (moist) at 19° and 766·3 mm. N = 10·45.
$C_9H_{11}ONBr_2,C_6H_3O_7N_3$ requires N = 10·41 per cent.

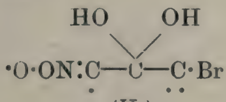
It was not found possible to determine the bromine in the picrate by the method of Carius owing to the explosion of the tube on heating.

Although the constitution of this dibromo-derivative so far as concerns the position of the bromine atoms has not been proved directly, its mode of formation and its general agreement in all characters with the nitro-haloid and di-iodo-derivatives of known constitution leave no doubt that the bromine atoms are in the positions 2 : 6. The dependence of colour upon the presence of the nitro-group is strikingly brought out in this case by the colourless hydrated (quinole) and anhydrous (quinonoid) forms. If, as may reasonably be assumed, one of the three molecules of water retained by the base is of the same function as the water of hydration in the dinitro-derivative, it appears that the two bromine atoms are sufficiently acid in character to enable the central carbon atom to retain the two hydroxyls:



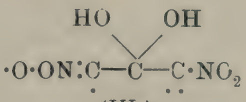
$$\mathrm{Br{\cdot}\underset{\cdot\cdot}{C}{-}\overset{HO\quad OH}{C}{-}\underset{\cdot\cdot}{C}{\cdot}Br}$$

(I.)



$$\mathrm{{\cdot}O{\cdot}ON{:}\underset{\cdot}{C}{-}\overset{HO\quad OH}{C}{-}\underset{\cdot\cdot}{C}{\cdot}Br}$$

(II.)



$$\mathrm{{\cdot}O{\cdot}ON{:}\underset{\cdot}{C}{-}\overset{HO\quad OH}{C}{-}\underset{\cdot\cdot}{C}{\cdot}NO_2}$$

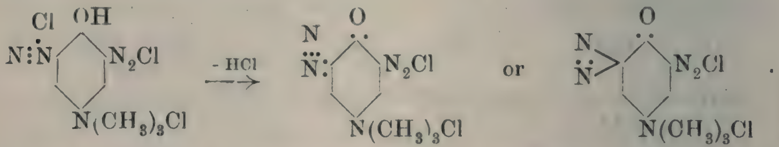
(III.)

The forms II and III, which represent coloured compounds, cannot be assumed by I. By the benzoylation of the dibromo-compound with benzoyl chloride and sodium hydroxide a product was obtained, the nature of which has not yet been fully made out, and the research requires extension also in this direction.

### 2 : 6-*Di-iodo*-4-*trimethylammonium*-1-*benzoquinone*.

This compound could not be conveniently prepared from the corresponding iodonitro-derivative by reduction and diazotisation of the iodoamino-base, because of the tendency of the reducing agents to remove the iodine atom. It was found unnecessary, however, to pursue this method further, as it was subsequently discovered that the diamino-derivative (T., 1912, **101**, 929) could readily be diazotised at both amino-groups with the formation of definite bisdiazonium salts. This property of the diaminotrimethylammonium-benzoquinone compounds is noteworthy in view of the fact that the amino-groups are in the meta-position. It is well known in diazo-chemistry that meta-diamines containing unprotected ortho- or para-positions can only be diazotised at a very low temperature in the presence of a great excess of acid. Even under these conditions the diazotisation is very imperfect so far as concerns one of the amino-groups, owing to the tendency of the diazonium salt to couple with a molecule of the undiazotised base with the formation of the aminoazo-derivative. In the present case the meta-amino-character of the molecule is completely modified by the presence of the trimethylammonium group.

In order to prepare the above compound, the dinitro-trimethylammonium derivative was completely reduced by tin and hydrochloric acid, the tin removed as sulphide, and the solution of the chloride, after concentration, diazotised in the usual way. The bisdiazonium salt in solution was decomposed by mixing with an excess of potassium iodide in aqueous solution and boiling as long as nitrogen was evolved. It is of interest to note that the solution of the chloride, which is at first colourless, becomes distinctly orange on diazotisation. It is most probable that the compound which is present in the solution is not simply the bisdiazonium salt, but an anhydride with one of the diazo-groups in the diazo-oxide (quinonediazide) form:



The addition of a concentrated solution of sodium dichromate to the diazotised solution causes the separation of a beautifully crystalline chromate (Meldola and Eynon, T., 1905, **87**, 1), but we have not yet ventured to investigate this compound on account of its violently explosive character.

The crude di-iodo-compound, prepared as above, was purified by crystallisation from hot water, with the addition of silver oxide in order to ensure the decomposition of any salt of the quinone-ammonium base contained in the solution. The substance separate on cooling in beautiful, silvery scales, which become opaque and fall to a crystalline powder on drying in the water-oven. The melting point of the dry compound is 189—190°:

0·2880 (oven-dried) gave 8·3 c.c. $N_2$ (moist) at 16·7° and 767·7 mm. N=3·38.

0·1985 (oven-dried) gave (by the method of Carius) 0·2312 AgI. I=62·92.

$C_9H_{11}ONI_2$ requires N=3·47; I=62·98 per cent.

The air-dried compound, like the corresponding dibromo-compound, contains 3 molecules of water, one of which is presumably of the same (quinole) function as the water of hydration of the dinitro- and bromonitro-compounds:

0·5091 (air-dried) lost, at 100°, 0·0596=11·70 $H_2O$.

$C_9H_{11}ONI_2,3H_2O-3H_2O$ requires a loss=11·82 per cent.

The base dissolves in hydrochloric acid with the formation of a chloride, but this salt was dissociable by water, and could not be isolated. Nitric acid displaces the iodine atoms, and, if sufficiently concentrated, reproduces the original dinitro-compound. The *picrate* was prepared from the base and picric acid in aqueous solution, and purified by crystallisation from alcohol. It consists of small, opaque, yellow needles, melting with decomposition at 193—194°:

0·1378 gave 10·4 c.c. $N_2$ (moist) at 15·5° and 759·6 mm. N = 8·81.

$C_9H_{11}ONI_2,C_6H_3O_7N_3$ requires N = 8·92 per cent.

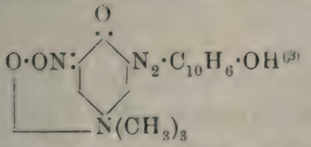
It will be observed that this di-iodo-derivative in both hydrated and anhydrous forms is also a colourless substance.

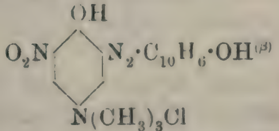
## *Nitroazo-derivatives.*

Dinitrotrimethylammonium-benzoquinone was reduced by ammonium sulphide, and the solution of the chloride of the nitroamino-base, obtained in the way previously described, was diazotised by the usual method. The solution of the diazonium salt, on mixing with an alkaline solution of β-naphthol, gave an immediate precipitate of a deep violet azo-compound. The latter was collected, washed, and dried. It was noticed that the deep violet colour of the freshly precipitated and semi-gelatinous azo-compound immediately changed to a bright scarlet on contact with hydrochloric acid, the violet colour being gradually restored on washing with water, and immediately on contact with alkali. From these remarkable colour changes, it was concluded that the quinonoid benzene nucleus still retained its basic character, notwithstanding the attachment of the azo-naphthol group. This conclusion was subsequently verified by the isolation of the chloride.

The azo-compound is sufficiently basic to dissolve in glacial acetic acid, but the acetate is dissociable by water. Advantage of this property was taken therefore in order to purify the substance, which was dissolved in hot glacial acetic acid; the solution, which was of an orange-red colour, was filtered, and then freely diluted with hot water. The azo-compound separated from the solution on cooling in small rosettes of bronzy needles. The latter were collected, washed with alcohol, and dried in the water-oven. Analysis indicated that the compound was the nitro-azo-derivative:

6-*Nitro-2-β-naphtholazo-4-trimethylammonium-1-benzoquinone.*





0·0944 gave 0·2148 $CO_2$ and 0·0412 $H_2O$. C = 62·06; H = 4·84.

0·0628 ,, 8·2 c.c. $N_2$ (moist) at 16° and 771·4 mm. N = 15·45.

$C_{19}H_{18}O_4N_4$ requires C = 62·26; H = 4·95; N = 15·34 per cent.

The azo-compound melts and decomposes above 300°. It is but very sparingly soluble in boiling alcohol, and imparts a beautiful violet colour to this solvent. It is non-phenolic in character, but dissolves in alcoholic sodium hydroxide with a violet colour, the solution becoming red and depositing scarlet crystals of the chloride on the addition of hydrochloric acid. The compound dissolves in concentrated sulphuric acid with a violet colour, which becomes red on dilution; it dissolves also in hot aniline with a bluish-violet colour. An air-dried specimen of the azo-compound underwent a loss on drying at 100°, indicating that the hydrated form is in this case also capable of existence, the loss in weight corresponding with rather more than that required for one molecule of water:

0·2492 lost $0·0148 = 5·94$.

$C_{19}H_{18}O_4N_4,H_2O - H_2O$ requires a loss $= 4·7$ per cent.

The hydrated crystals fall to a bronzy, crystalline powder, but otherwise undergo no great change in appearance.

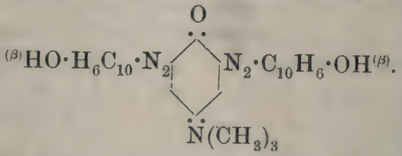
The *chloride* (formulated above) was prepared by adding excess of hydrochloric acid to the hot solution of the azo-compound in glacial acetic acid, and allowing the salt to crystallise out. It consists of brick-red needles, which can be safely washed with alcohol and dried in the water-oven without undergoing dissociation:

0·1254 gave 14·4 c.c. $N_2$ (moist) at 15·5° and 763·1 mm. $N = 13·47$.
0·2970 ,, 0·1034 AgCl. $Cl = 8·61$.

$C_{19}H_{19}O_4N_4Cl$ requires $N = 13·91$; $Cl = 8·80$ per cent.

(The chlorine was determined by decomposing the salt with warm, dilute ammonia, collecting the free azo-compound, and precipitating the silver chloride from the filtrate acidified with nitric acid in the usual way.)

Of the diazo-compounds belonging to this series we have prepared the type containing the two azonaphthol groups:



This and analogous compounds will be made the subjects of further investigation.

We desire to express our thanks to Mr. Robert O. Bishop, who has rendered us valuable assistance in connexion with the analytical part of the work.

City and Guilds of London Institute,
Finsbury Technical College.

# XXIII.—*The Constituents of the Rhizome and Roots of* Caulophyllum thalictroides.

By **Frederick Belding Power** and **Arthur Henry Salway.**

*Caulophyllum thalictroides* (Linné), Michaux (Nat. Ord., *Berberidaceæ*), commonly known, among other names, as "Blue Cohosh," is a plant indigenous to North America, and is the only known species of the genus. Although the rhizome and roots of this plant, or preparations therefrom, are considerably employed in medicine, the drug is not at present recognised by any of the national Pharmacopœias.

Caulophyllum appears to have been first chemically examined by F. F. Mayer (*Amer. J. Pharm.*, 1863, **35**, 99), who stated it to contain a saponaceous principle and a colourless alkaloid, although the latter was not actually isolated. A. E. Ebert (*ibid.*, 1864, **36**, 203) also observed the presence of a substance analogous to saponin, but failed to obtain an alkaloid. It was, however, definitely shown by J. U. Lloyd ("Drugs and Medicines of North America," Vol. II., 1887, p. 153, and *Proc. Amer. Pharm. Assoc.*, 1893, **41**, 115) that caulophyllum contains an appreciable amount of an alkaloid, which he designated "caulophylline," but its composition was not determined. Although he did not succeed in crystallising the base, the hydrochloride was described as forming acicular crystals. The present authors have obtained the respective alkaloid in a pure, crystalline state, and have proved it to be methylcytisine.

A saponin-like substance was also isolated from caulophyllum by Lloyd (*loc. cit.*, 1887, p. 151), who was the first to obtain it in a crystalline and apparently pure state, and found it to be a glucoside. This compound, the general properties of which were described, was termed "leontin," with reference to an old botanical name (*Leontice*) of the plant. Several analyses of the substance, conducted by H. Trimble, led the latter to assign to it the formula $C_{16}H_{26}O_5,H_2O$. Although from the results of the present investigation the percentage composition of the compound appears to have been accurately determined, thus affording evidence of its purity, yet the formula deduced therefrom is incorrect. A consideration of the products of hydrolysis, which have now for the first time been determined, has shown the compound to be represented by the formula $C_{54}H_{88}O_{17},4H_2O$, and it is proposed to designate it *caulosaponin*. It has, furthermore, been shown that caulophyllum contains a second saponin-like glucoside, which, although present in much smaller proportion than that above mentioned, has also been obtained in a crystalline state and completely characterised. It possesses the formula $C_{66}H_{104}O_{17}$, and has been termed *caulophyllosaponin.*

Gilbard (*Analyst*, 1911, **36**, 270) has suggested a test for the identification of the so-called "caulophyllin," an impure resinous product obtained from caulophyllum, which is used to some extent medicinally. The colour reaction upon which this test depends is due to the presence of the above-mentioned glucosides.

A summary of the substances isolated in the present investigation, and their derivatives, together with some physiological tests, is given at the end of this paper.

## EXPERIMENTAL.

The material employed for this investigation consisted of the rhizome and roots of *Caulophyllum thalictroides* (Linné), Michaux. It was perfectly authentic, having been specially gathered in North Carolina, and kindly supplied to us by Professor J. U. Lloyd, of Cincinnati, Ohio, to whom our best thanks may here be expressed.

A small portion (10 grams) of the material was first tested for the presence of an alkaloid, and with a positive result.

In order to ascertain whether an enzyme were present, 100 grams of the ground material were macerated with water at the ordinary temperature for two days. To the expressed and filtered liquid about twice its volume of alcohol was added, when a gelatinous precipitate was produced. This was collected, washed with a little alcohol, and dried in a vacuum over sulphuric acid, when it amounted to 0·3 gram. It gave the biuret reaction, and slowly hydrolysed amygdalin, thus proving the presence of an enzyme.

Another portion (25 grams) of the ground material was completely extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

| | | | | | |
|---|---|---|---|---|---|
| Petroleum (b. p. 35—50°) | extracted | 0·15 | gram | = 0·60 | per cent. |
| Ether | ,, | 0·65 | ,, | = 2·60 | ,, |
| Chloroform | ,, | 0·81 | ,, | = 3·24 | ,, |
| Ethyl acetate | ,, | 0·42 | ,, | = 1·68 | ,, |
| Alcohol | ,, | 4·90 | ,, | =19·60 | ,, |
| Total ……… | | 6·93 | grams | =27·72 | per cent. |

For the purpose of a complete examination, 22·37 kilograms of the ground material were completely extracted with hot alcohol, when, after the removal of the greater portion of the alcohol, 8·28 kilograms of a dark-coloured, viscid extract were obtained.

Two kilograms of the above-mentioned extract were mixed with water, and the mixture distilled in a current of steam. The distillate was extracted with ether, and the solvent removed, when about 1 gram of a pale yellow essential oil was obtained. This had a pleasant odour, and yielded the colour reaction for furfuraldehyde.

After the above operation there remained in the distillation flask a dark-coloured aqueous liquid (A), which contained in suspension a considerable quantity of grey, amorphous material (B), and, on cooling, the whole formed a soft, gelatinous mass. The separation of the amorphous material from the aqueous liquid was effected by agitating the mixture with hot amyl alcohol, which dissolved all the solid substance, with the exception of a very small amount of indefinite material which was removed by filtration. The amyl alcohol extract was subsequently washed with water, the washings being added to the main portion of the aqueous liquid.

### *Examination of the Aqueous Liquid* (A).

The aqueous liquid, which had been treated with amyl alcohol as above described, was next extracted many times with ether. The ethereal liquids were united, washed, dried, and the solvent removed, when 2 grams of a viscid, brown residue were obtained. This was agitated with alcohol, when a sparingly soluble solid separated, which, when crystallised from a mixture of pyridine and alcohol, was obtained in colourless leaflets, melting and decomposing at 275—280°. The substance yielded an acetyl derivative melting at 169°, which, together with its colour reactions, indicated it to be citrullol, $C_{23}H_{45}O_2(OH)_3$. It was subsequently obtained in larger amount from an ethereal extract of the above-mentioned grey, amorphous material, and was then completely identified.

The aqueous liquid, after extraction with ether as above described, frothed strongly on agitation, and evidently contained some saponin-like substance which had not been removed by the previous treatment with amyl alcohol. With the object of effecting the complete removal of this substance, the aqueous liquid was again shaken repeated with hot amyl alcohol, these extracts being then united, washed with a little water, and the solvent removed by distillation under diminished pressure. A quantity (25 grams) of a dark brown solid was thus obtained, which was glucosidic, and possessed the characters of a saponin. It was dissolved in alcohol, and the solution kept for some time, when a colourless, crystalline substance separated, which, after recrystallisation from alcohol, melted and decomposed at 250—255°. This compound was found to be identical with a glucoside which was obtained in larger amount from the amorphous material extracted by the first treatment of the aqueous liquid with amyl alcohol, and has been designated *caulosaponin*. It is fully described in connection with the examination of the grey, amorphous product (B).

The aqueous liquid was next treated with a slight excess of basic lead acetate, which produced a relatively small amount of a dark brown precipitate. This was collected, washed, suspended in water, and decomposed by hydrogen sulphide, but no definite substance could be isolated from it. The filtrate from the basic lead acetate precipitate was deprived of lead by means of hydrogen sulphide, and the clear, filtered liquid concentrated under diminished pressure to a convenient volume. It then readily responded to the tests for an alkaloid, and was also found to contain a quantity of reducing sugar. From a small portion of the liquid, *d*-phenylglucosazone (m. p. 210°) was prepared.

### *Isolation of Methylcytisine*, $C_{11}H_{13}ON_2(CH_3)$.

In order to isolate the alkaloid from the above-mentioned aqueous liquid, the entire remaining portion of the latter was made alkaline with sodium hydroxide and repeatedly extracted with chloroform. The chloroform extracts were united, washed with a little water, dried, and the solvent removed, when about two grams of a viscid, brown residue were obtained, which gave the reactions for an alkaloid. For the purpose of purifying this material, it was dissolved in dry chloroform, and a current of dry hydrogen chloride passed into the solution, when a colourless hydrochloride of the base was precipitated. This was collected, and crystallised from a mixture of alcohol and ethyl acetate, when it separated in colourless prisms, decomposing at 250—255°. The air-dried substance was analysed with the following results:

0·0967 gave 0·1726 $CO_2$ and 0·0594 $H_2O$. C=48·7; H=6·8.
0·1212 „ 10·3 c.c. $N_2$ at 20° and 757 mm. N=9·7.
0·1105 „ 0·1078 AgCl. Cl=24·1.

$C_{12}H_{18}ON_2Cl_2,H_2O$ * requires C=48·8; H=6·8; N=9·5; Cl=24·1 per cent.

In order to obtain the free base, the hydrochloride was dissolved in a little water, the solution made alkaline with sodium hydroxide, and then extracted six times with chloroform. The united chloroform extracts were washed with a very small quantity of water, then dried, and the solvent removed. The residue, which soon solidified, was recrystallised from a mixture of benzene and light petroleum, when the base was obtained in colourless, prismatic needles, melting at 137°. For the purpose of its complete examination, the entire remaining portion of the original alcoholic extract of the drug was worked up in the manner already described. The total amount of pure alkaloid thus obtained, calculated as the free base, was about 5 grams. It was analysed, and its molecular weight determined, with the following results:

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* The water of crystallisation in this salt could not be directly determined, since the substance slowly loses hydrogen chloride on dehydration.

0·1076 gave 0·2794 $CO_2$ and 0·0780 $H_2O$. C = 70·8; H = 8·0.
0·1122 „ 13·4 c.c. $N_2$ at 21° and 762 mm. N = 13·6.
0·4666, in 27·23 benzene, gave $\Delta t - 0{\cdot}387°$. M.W. = 221.
$C_{12}H_{16}ON_2$ requires C = 70·6; H = 7·8; N = 13·7 per cent. M.W. = 204.

The alkaloid was optically active, and a determination of its specific rotatory power gave the following result:

0·2256, made up to 20 c.c. with water, gave $\alpha_D$ − 5°0′ in a 2-dcm. tube, whence $[\alpha]_D$ − 221·6°.

A small amount of the alkaloid was dissolved in a known volume of *N*/10-sulphuric acid, and the excess of the latter titrated with *N*/10-barium hydroxide, using iodoeosin as indicator in the presence of ether.

0·1305 neutralised 6·4 c.c. *N*/10-$H_2SO_4$, which is the theoretical amount required for $C_{12}H_{16}ON_2$ as a monacidic base.

The alkaloid was readily soluble in water, alcohol, chloroform, or benzene, but less readily in ether. The aurichloride was obtained in golden-yellow needles, which decomposed at 205°.

0·1550 gave 0·1512 $CO_2$, 0·0443 $H_2O$, and 0·0561 Au. C = 26·6; H = 3·2; Au = 36·2.
$C_{12}H_{17}ON_2,AuCl_4$ requires C = 26·5; H = 3·1; Au = 36·2 per cent.

The composition of the above-described alkaloid and its salts, together with its general characters, indicated it to be methylcytisine. This compound had not hitherto been known to occur in nature, although it has previously been prepared by the methylation of cytisine, $C_{11}H_{14}ON_2$, an alkaloid found in the common laburnum (*Cytisus Laburnum*, Linné) and other species of *Cytisus*, as well as in various other plants. It represents the alkaloid previously obtained by J. U. Lloyd (*Proc. Amer. Pharm. Assoc.*, 1893, **41**, 115), and designated by him "caulophylline," as its composition had not then been determined. Methylcytisine *picrate* appears not to have previously been prepared. This salt crystallised from hot water in long, yellow needles, which sintered at about 200°, and melted completely at 228°.

Although the characters of the above-described alkaloid were in quite complete agreement with those of methylcytisine, as recorded in the literature (compare Buchka and Magalhæs,* *Ber.*, 1891, **24**, 678; Partheil, *Arch. Pharm.*, 1892, **230**, 448; and Rauwerda, *ibid.*, 1900, **238**, 484), a small amount of the latter compound was prepared from a commercial specimen of cytisine for the purpose of comparison. It melted at 135°, and when mixed with the alkaloid from caulophyllum no depression of the melting point ensued. The identification of the last-mentioned alkaloid as methylcystisine was thus completely effected.

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* The melting point of 245°, as given by Buchka and Magalhæs (*loc. cit.*), for methylcytisine, is obviously an error.

*Quantitative Determination of the Alkaloid in Caulophyllum.*—Having determined the composition and characters of the alkaloid in caulophyllum, it seemed desirable to formulate a method for ascertaining the proportion in which it exists in the drug. The following method of procedure was found to give satisfactory results:

Twenty grams of caulophyllum, in No. 60 powder, were introduced into a suitable flask, 100 c.c. of chloroform and 10 c.c. of aqueous sodium carbonate (10 per cent. solution) added, and the whole was vigorously shaken from time to time during a period of four hours. The mixture was then filtered, and 50 c.c. of the chloroform liquid (=10 grams of caulophyllum) transferred to a separator, in which it was vigorously shaken with 10 c.c. of *N*/10-sulphuric acid. After separating the acid liquid from the chloroform, the latter was again shaken with 10 c.c. of *N*/10-sulphuric acid. The two portions of acid liquid were united, extracted with 20 c.c. of ether, which removed a small quantity of emulsified chloroform, then made alkaline by the addition of 5 c.c. of aqueous sodium carbonate (10 per cent. solution), and agitated with three successive portions of chloroform of 20 c.c. each. The united chloroform extracts were washed twice with water, using each time 2 c.c. of the latter, and the chloroform then carefully removed by distillation. The residual alkaloid was dissolved in 10 c.c. of *N*/50-sulphuric acid, 10 c.c. of ether added, the solution transferred to a stoppered bottle, and the excess of sulphuric acid determined by titration with *N*/50-barium hydroxide, using iodoeosin as the indicator. It was thus found that 2·1 c.c. *N*/50-sulphuric acid were required to neutralise the alkaloid, and as it has already been shown that methylcytisine, $C_{12}H_{16}ON_2$, under the above conditions of titration, possesses the character of a monacidic base, the corresponding amount of alkaloid would be 2·1 × 0·00408 or 0·0086 gram. This is equivalent to 0·086 per cent. of methylcytisine in the drug.

In a second assay of the caulophyllum, the digestion with chloroform and aqueous sodium carbonate was prolonged for twenty hours, but the process was otherwise conducted as before. The amount of alkaloid thus obtained was equivalent to 0·078 per cent. of the drug, and the two determinations may therefore be considered to agree within the limits of experimental error. From this result it was also apparent that the digestion of the drug for a period of more than four hours presents no advantage.

The accuracy of the above-described method for the quantitative determination of the alkaloid was controlled by dissolving 0·0098 gram of pure methylcytisine in 50 c.c. of chloroform, and treating this solution in precisely the same manner as the chloroform extract of the drug. The amount of alkaloid indicated by the final titration was 0·0096 gram.

### *Examination of the Grey, Amorphous Material* (B).

As previously noted, the aqueous liquid remaining after the distillation of the original alcoholic extract with steam contained a quantity of grey, amorphous material in suspension, which was removed by extraction with hot amyl alcohol. This amyl alcohol solution was concentrated to a small bulk under diminished pressure, and a large volume of ether added, which precipitated a greyish-white solid.

### *Isolation of a Crystalline Glucoside, Caulosaponin,* $C_{54}H_{88}O_{17},4H_2O$.

The above-mentioned greyish-white solid was collected, and amounted to 94 grams. It was dissolved in hot alcohol, and the solution kept for some time, when a crystalline, glucosidic substance was deposited. This was crystallised several times from alcohol, and was finally obtained in colourless, slender needles, melting and decomposing at 250—255°. The amount of pure substance isolated from 2 kilograms of the original alcoholic extract was 16 grams. For the purpose of its complete examination, a further and larger quantity was subsequently obtained by working up the remainder of the alcoholic extract in the manner already described:

0·1173, when heated at 115°, lost 0·0077 $H_2O$. $H_2O = 6·6$.
0·1017 * gave 0·2394 $CO_2$ and 0·0796 $H_2O$. C = 64·2; H = 8·7.
0·1074 * „ 0·2520 $CO_2$ „ 0·0836 $H_2O$. C = 64·0; H = 8·6.
$C_{54}H_{88}O_{17},4H_2O$ requires $H_2O = 6·7$ per cent.
$C_{54}H_{88}O_{17}$ requires C = 64·3; H = 8·7 „ „

A comparison of the composition and properties of this compound with those of the glucoside previously isolated by J. U. Lloyd, and described by him under the name of "leontin" (Drugs and Medicines of North America," Vol. II., 1887, p. 151), renders it evident that the substances are identical. In view of the fact, however, that the compound has now been completely characterised, and that, by an examination of its hydrolytic products, it has been shown to possess the formula $C_{54}H_{88}O_{17},4H_2O$, instead of $C_{16}H_{26}O_5,H_2O$, as originally assigned to it (*loc. cit.*), it is deemed desirable to give it the new and distinctive name of *caulosaponin*. This is the more important as the name "leontin" appears also to have been given to a preparation of caulophyllum which does not represent the pure glucoside.

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* Anhydrous substance.

*Caulosaponin*, $C_{54}H_{88}O_{17},4H_2O$, is insoluble in water, ether, chloroform, or benzene, but is moderately soluble in hot alcohol, although sparingly so in cold. It possesses phenolic properties, and dissolves readily in solutions of the alkali hydroxides. When the substance is dissolved in acetic anhydride, a little chloroform added, and subsequently a few drops of concentrated sulphuric acid, a purplish-red coloration is produced, which gradually fades. A solution of caulosaponin in water containing a little alcohol yields, on agitation, an abundant and persistent froth, and the substance is therefore a member of that class of compounds which have been designated as saponins. So far as known to us, only one other well-characterised substance of this class has previously been obtained in a crystalline form (compare *Arch. Pharm.*, 1912, **250**, 427).

*Deca-acetylcaulosaponin*, $C_{54}H_{78}O_{17}(CO{\cdot}CH_3)_{10}$.—This derivative of caulosaponin was prepared by heating the latter with acetic anhydride for two hours. The mixture was then poured into water, and the precipitated solid collected, washed, and dried in a vacuum desiccator over sulphuric acid and solid potassium hydroxide. The product was thus obtained as a white powder, which melted at 135—140°. It was readily soluble in the usual organic solvents, but could not be crystallised:

0·1323 gave 0·3017 $CO_2$ and 0·0899 $H_2O$. C = 62·2; H = 7·6.

$C_{74}H_{108}O_{27}$ requires C = 62·2; H = 7·6 per cent.

It is thus evident that caulosaponin contains ten hydroxyl groups.

### *Hydrolysis of Caulosaponin.*

### *Formation of Caulosapogenin*, $C_{42}H_{62}O_2(OH)_4$, *and Dextrose.*

Twenty grams of caulosaponin were dissolved in 500 c.c. of alcohol, then 150 c.c. of a 10 per cent. aqueous solution of hydrogen chloride added, and the mixture heated on a water-bath for several hours, when a crystalline hydrolytic product separated from the hot liquid. After removal of the alcohol in a current of steam, the mixture was filtered, the filtrate being set aside for the subsequent examination of the sugar. The crystalline product was well washed with water, and purified by recrystallisation from dilute pyridine. It was thus obtained in colourless, anhydrous, rhombohedral prisms, which decomposed at about 315°:

0·0893 gave 0·2474 $CO_2$ and 0·0806 $H_2O$. C = 75·6; H = 10·0.

0·0791 „ 0·2195 $CO_2$ „ 0·0716 $H_2O$. C = 75·7; H = 10·1.

$(C_7H_{11}O)_x$ requires C = 75·7; H = 9·9 per cent.

The molecular weight of the above-described compound could not be directly determined on account of its sparing solubility in suitable solvents. An examination of its derivatives showed, however, that it possesses the formula $C_{42}H_{66}O_6$, and that it contains four hydroxyl groups, one of which is phenolic. As it is a new compound, it is proposed to designate it *caulosapogenin.*

*Caulosapogenin*, $C_{42}H_{62}O_2(OH)_4$, is insoluble in water, chloroform, or benzene, and sparingly soluble in absolute alcohol, but more readily so in alcohol containing a little water. It also dissolves in aqueous alkali hydroxides in the presence of alcohol, and is therefore phenolic in character. When caulosapogenin is dissolved in acetic anhydride, a little chloroform added, and subsequently a few drops of concentrated sulphuric acid, a rose-red coloration is produced which gradually disappears. When a solution of the substance in aqueous alcohol is agitated, a copious frothing is produced, but the permanency of the latter is not so great as in the case of the glucoside itself.

*Tetra-acetylcaulosapogenin*, $C_{42}H_{62}O_6(CO{\cdot}CH_3)_4$.—This compound was prepared by heating caulosapogenin for some time with acetic anhydride, the solution being then concentrated and poured into water. The product, which soon solidified, was collected, washed well with water, and dried over sulphuric acid and solid potassium hydroxide, when it formed a white, amorphous powder, which melted at 120°. It was extremely soluble in the usual organic solvents, but could not be crystallised:

0·1040 gave 0·2743 $CO_2$ and 0·0866 $H_2O$. C = 71·9; H = 9·2.

$C_{50}H_{74}O_{10}$ requires C = 71·9; H = 8·9 per cent.

*Diacetylcaulosapogenin*, $C_{42}H_{64}O_6(CO{\cdot}CH_3)_2$.—The above-described tetra-acetyl derivative, when heated with ammonium carbonate in the presence of alcohol, readily loses two acetyl groups. The resulting *diacetyl* compound crystallises from dilute alcohol in thin, colourless needles, which melt at 160—162°:

0·1221 gave 0·3288 $CO_2$ and 0·1036 $H_2O$. C = 73·4; H = 9·4.

$C_{46}H_{70}O_8$ requires C = 73·6; H = 9·3 per cent.

Diacetylcaulosapogenin possesses phenolic properties, and yields a crystalline sodium derivative.

*Diacetylmonosodiocaulosapogenin*, $C_{42}H_{63}O_6Na(CO{\cdot}CH_3)_2$.—This compound is best prepared by agitating an ethereal solution of tetra-acetyl- or diacetyl-caulosapogenin with aqueous sodium carbonate, when the *sodium* derivative separates in colourless needles:

0·1818, when heated at 115°, lost 0·0094 $H_2O$. $H_2O$ = 5·2.

0·1488 * gave 0·0138 $Na_2SO_4$. Na = 3·0.

$C_{46}H_{69}O_8Na,2H_2O$ requires $H_2O$ = 4·5 per cent.

$C_{46}H_{69}O_8Na$ requires Na = 3·0 per cent.

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* Anhydrous substance.

The number of acetyl groups in this sodium derivative was directly determined by heating the substance with a known volume of $N/10$-alcoholic sodium hydroxide, and titrating the excess of alkali with standard acid:

0·3191 gave on hydrolysis acetic acid equivalent to 8·45 c.c. $N/10$-NaOH. $CO{\cdot}CH_3=11{\cdot}4$.

$C_{42}H_{63}O_6Na(CO{\cdot}CH_3)_2$ requires $CO{\cdot}CH_3=11{\cdot}1$ per cent.

*Tetrabenzoylcaulosapogenin*, $C_{42}H_{62}O_6(CO{\cdot}C_6H_5)_4$.—This compound was prepared by heating caulosapogenin in pyridine solution with benzoyl chloride for about an hour. The mixture was then poured into water, rendered slightly alkaline with sodium carbonate, and kept for some time, when the reaction product slowly solidified. It was collected and purified by crystallisation from a mixture of chloroform and alcohol, when the substance separated in well-formed, hexagonal prisms, melting at 288°. An analysis and a determination of its molecular weight gave the following results:

0·1040 gave 0·2946 $CO_2$ and 0·0735 $H_2O$. $C=77{\cdot}3$; $H=7{\cdot}9$.

0·5529 in 25·2 benzene gave $\Delta t - 0{\cdot}102°$. M.W. = 1076.

$C_{70}H_{82}O_{10}$ requires $C=77{\cdot}6$; $H=7{\cdot}6$ per cent. M.W. = 1082.

The preceding results have thus served to establish the correctness of the formula assigned to caulosapogenin.

*Tetrabenzoylcaulosapogenin* is readily soluble in ether, chloroform, or benzene, but only sparingly so in water or alcohol. It does not possess the phenolic properties of the original substance. Its specific rotatory power was determined, with the following result:

0·3092, made up to 20 c.c. with chloroform, gave $\alpha_D +3°26'$ in a 2-dcm. tube, whence $[\alpha]_D +111{\cdot}0°$.

*Caulosapogenin Monomethyl Ether*, $C_{42}H_{65}O_5(O{\cdot}CH_3)$.—This substance was prepared by heating caulosapogenin for several hours with alcoholic sodium hydroxide and methyl iodide. When crystallised from dilute alcohol, it separated in well-formed needles, melting at 235°:

0·1143 gave 0·3173 $CO_2$ and 0·1059 $H_2O$. $C=75{\cdot}7$; $H=10{\cdot}3$.

The number of methoxyl groups in the compound was determined by Perkin's modification of Zeisel's method:

0·1318 gave 0·0544 AgI. $MeO=5{\cdot}5$.

$C_{42}H_{65}O_5(OMe)$ requires $C=75{\cdot}9$; $H=10{\cdot}0$; $MeO=4{\cdot}6$ per cent.

The specific rotatory power of the substance was determined with the following result:

0·1412, made up to 20 c.c. with chloroform, gave $\alpha_D +1°3'$ in a 2-dcm. tube, whence $[\alpha]_D +74{\cdot}4°$.

### *Oxidation of Caulosapogenin.*

With the object of obtaining further information respecting the nature of caulosapogenin, a quantity (10 grams) of the latter was dissolved in aqueous potassium hydroxide with the addition of a little pyridine, and a 4 per cent. solution of potassium permanganate gradually added, the mixture being heated on a water-bath. The oxidation proceeded rapidly at first, but after the addition of about 400 c.c. of the permanganate solution (about 10 atomic proportions of oxygen) the latter was only slowly decolorised. The mixture was then filtered under pressure, and the alkaline liquid extracted with ether, but nothing was thus removed. On subsequently acidifying the liquid, a voluminous precipitate was produced, which was collected, washed with water, and then dissolved in ether. The ethereal liquid, on keeping a short time, deposited a crystalline, acidic substance, which was recrystallised from dilute alcohol. It separated from this solvent in thin, colourless needles, which decomposed at 310°. An analysis and a determination of the molecular weight gave the following results:

0·1096 gave 0·2191 $CO_2$ and 0·0922 $H_2O$. C = 72·7; H = 9·3.

0·1606 in 25·75 acetic acid gave $\Delta t - 0{\cdot}093°$. M.W. = 261.

$C_{16}H_{24}O_3$ requires C = 72·7; H = 9·1 per cent. M.W. = 264.

0·1075 neutralised 4·15 c.c. $N/10$-NaOH.

A monocarboxylic acid, $C_{16}H_{24}O_3$, requires 4·10 c.c. $N/10$-NaOH.

Since the above-described *acid*, $C_{16}H_{24}O_3$, does not agree in its properties with any acid of this formula which has heretofore been recorded, it is evidently a new compound, but the amount obtained was too small to permit of its further examination. It may, however, be concluded that the oxidation of caulosapogenin with potassium permanganate effects a far-reaching degradation of the molecule.

### *Examination of the Sugar yielded by the Hydrolysis of Caulosaponin.*

The aqueous acid liquid resulting from the hydrolysis of the glucoside caulosaponin, as above described, was exactly neutralised with sodium carbonate, and evaporated to dryness under diminished pressure. The residue was then digested with hot alcohol, the mixture filtered, and the filtrate concentrated, when a viscid syrup was obtained. The latter yielded *d*-phenylglucosazone, which, after crystallisation from dilute pyridine, melted and decomposed at 212°.

The above results have thus shown that caulosaponin is resolved on hydrolysis into caulosapogenin and dextrose. A known quantity of the glucoside, when hydrolysed by dilute hydrochloric acid in the presence of alcohol, and the alcohol subsequently removed, yielded 64·1 per cent. of its weight of caulosapogenin ($C_{54}H_{88}O_{17}$ requires $C_{42}H_{66}O_6 = 66·1$ per cent.). The hydrolysis of caulosaponin therefore takes place according to the equation:

$$C_{54}H_{88}O_{17} + H_2O = C_{42}H_{66}O_6 + 2C_6H_{12}O_6.$$

The amyl-alcoholic liquid, from which the caulosaponin had been separated by treatment with ether, as above described, was brought on to purified sawdust, the mixture thoroughly dried, and then extracted successively in a large Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

### *Petroleum Extract of the Amorphous Material* (B).

This was a dark coloured, fatty product, amounting to 49 grams. It was hydrolysed by heating for a short time with an alcoholic solution of potassium hydroxide, after which the alcohol was removed, water added, and the alkaline mixture extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when 11 grams of a viscid residue were obtained.

### *Isolation of a Phytosterol*, $C_{27}H_{46}O$.

The above-mentioned residue of unsaponifiable material was digested with cold alcohol, which removed a quantity of gummy matter, leaving a crystalline solid undissolved. The latter was collected, and, after several crystallisations from ethyl acetate, was obtained in colourless leaflets, melting at 153°. The substance gave the colour reaction of the phytosterols, and evidently belonged to that class of compounds:

0·0918* gave 0·2812 $CO_2$ and 0·1002 $H_2O$. $C = 83·5$; $H = 12·1$.

$C_{27}H_{46}O$ requires $C = 83·9$; $H = 11·9$ per cent.

### *Examination of the Fatty Acids.*

The aqueous alkaline liquid which had been extracted with ether for the removal of the unsaponifiable material, as above described, was acidified with dilute sulphuric acid, and again extracted with ether. After the removal of the solvent, the residual fatty acids were converted into their lead salts, and the latter treated with ether. The soluble portion, when decomposed by hydrochloric acid, yielded 18 grams of liquid acids, whilst the insoluble portion gave about 5 grams of solid acids.

*The Liquid Acids.*—These acids were distilled under diminished pressure, and passed over at 210—245°/15 mm. as a pale yellow oil. An analysis and a determination of the neutralisation and iodine values gave the following results:

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* Dried at 110°.

0·1176 gave 0·3310 $CO_2$ and 0·1264 $H_2O$. C = 76·8; H = 11·9.
Neutralisation value = 199·1; Iodine value = 159.
$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. N.V. = 198·9; I.V. = 90·1.
$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent. N.V. = 200·4; I.V. = 181·4.

It would appear from these results that the liquid acids consisted of a mixture of oleic and linolic acids.

*The Solid Acids.*—These acids were converted into the methyl ester, and the latter separated by distillation under diminished pressure into two fractions, one of which was collected at 200—205°, and the other above 205°/20 mm. The first fraction yielded, on hydrolysis, a product which melted at 55—56°, and had a neutralisation value of 214; it evidently consisted of a mixture of palmitic and stearic acids. The fraction of ester distilling above 205°/20 mm. gave, on hydrolysis, an acid which separated from hot ethyl acetate in small leaflets, melting at 75—76°, and was identified as cerotic acid (Found, C = 78·6; H = 13·3. Calc., C = 78·8; H = 13·1 per cent.).

### *Ethereal Extract of the Amorphous Material* (B).

### *Isolation of Citrullol*, $C_{28}H_{45}O_2(OH)_3$.

The ethereal extract was a greyish-white powder, and amounted to 71 grams. It was dissolved in hot alcohol, and the solution kept for some time, when a small quantity of a sparingly soluble substance slowly separated. The latter was collected and crystallised from a mixture of pyridine and alcohol, when it was obtained in colourless leaflets, melting and decomposing at about 275—280°. The substance gave the colour reactions of ipuranol and allied alcohols, and yielded an acetyl derivative melting at 169—170°. These properties, together with an analysis of the substance (Found, C = 71·9; H = 10·4. Calc., C = 72·4; H = 10·3 per cent.), proved its identity with citrullol, $C_{28}H_{48}O_5$ (compare T., 1910, **97**, 102; and P., 1912, **28**, 318).

### *Isolation of a New Crystalline Glucoside, Caulophyllosaponin*, $C_{66}H_{104}O_{17}$.

The alcoholic liquid remaining after the separation of the above-described citrullol was heated on a water-bath, and water gradually added until turbidity ensued, when a crystalline solid separated on cooling. Some difficulty was experienced in purifying this substance, owing to the presence of small quantities of citrullol and caulosaponin, but after a process of fractional crystallisation from dilute alcohol it was obtained in colourless, silky needles, melting and decomposing at 250—260°. The substance was glucosidic and anhydrous. It was analysed, with the following results:

0·1129 gave 0·2803 $CO_2$ and 0·0916 $H_2O$. C = 67·7; H = 9·0.
0·1050 ,, 0·2611 $CO_2$ ,, 0·0880 $H_2O$. C = 67·8; H = 9·3.
$C_{66}H_{104}O_{17}$ requires C = 67·8; H = 8·9 per cent.

These results, together with the data subsequently obtained by an examination of the hydrolytic products of the glucoside, showed it to possess the formula $C_{66}H_{104}O_{17}$. As no glucoside of this formula has hitherto been recorded, it is proposed to designate the above-described compound *caulophyllosaponin*, with reference to the source from which it has been obtained, and the fact that it has the properties of a saponin. For its complete examination, the amount obtained from the total (8·28 kilograms) original alcoholic extract of the drug was employed.

*Caulophyllosaponin*, $C_{66}H_{104}O_{17}$, is extremely soluble in alcohol, sparingly so in ether, and insoluble in water. It dissolves in solutions of the alkali hydroxides, and possesses phenolic properties. A solution of the substance in water containing a little alcohol yields, on agitation, an abundant and persistent froth. When the substance is dissolved in acetic anhydride, a little chloroform added, and subsequently a few drops of concentrated sulphuric acid, a purplish-red colour is produced, quite analogous to that yielded under the same conditions by caulosaponin.

The specific rotatory power of caulophyllosaponin was determined, with the following result:

0·1600, made up to 20 c.c. with absolute alcohol, gave $\alpha_D$ +0°31′ in a 2-dcm. tube, whence $[\alpha]_D$ +32·3°.

*Deca-acetylcaulophyllosaponin*, $C_{66}H_{94}O_{17}(CO{\cdot}CH_3)_{10}$.—This derivative of caulophyllosaponin was prepared by heating it for some time with acetic anhydride, removing the greater part of the latter by distillation, and then pouring the residue into water. An amorphous, white solid was thus deposited, which was extremely soluble in organic solvents, and could not be crystallised. It was first dried in a vacuum desiccator over sulphuric acid and solid potassium hydroxide, and then at 110°, when it melted at 155—160°:

0·1503 gave 0·3565 $CO_2$ and 0·1074 $H_2O$. C = 64·7; H = 7·9.
$C_{86}H_{124}O_{27}$ requires C = 65·0; H = 7·8 per cent.

### *Hydrolysis of Caulophyllosaponin.*

### *Formation of Caulophyllosapogenin,* $C_{56}H_{82}O_3(OH)_6$, *and Arabinose.*

The hydrolysis of caulophyllosaponin was affected by heating the latter with a 5 per cent. solution of hydrogen chloride in aqueous alcohol for several hours. The alcohol was then removed in a current of steam, and the hydrolytic product, which had separated from the hot liquid in a crystalline state, was collected, the aqueous liquid being put aside for the subsequent examination of the sugar. The crystalline hydrolytic product was recrystallised from dilute pyridine, when it separated in rhombohedral prisms, which decomposed at about 315°:

0·0981 gave 0·2670 $CO_2$ and 0·0862 $H_2O$. C=74·2; H=9·8.
0·1013 ,, 0·2748 $CO_2$ ,, 0·0900 $H_2O$. C=74·0; H=9·9.
$C_{56}H_{88}O_9$ requires C=74·3; H=9·7 per cent.

The molecular formula of the above hydrolytic product was established by means of the derivatives described below. It has thus been definitely shown to possess the formula $C_{56}H_{88}O_9$, and to contain six hydroxyl groups, two of which are phenolic. As it is a new compound, it is proposed to designate it *caulophyllosapogenin.*

*Caulophyllosapogenin*, $C_{56}H_{82}O_3(OH)_6$, possesses physical properties which are very similar to those of the previously described hydrolytic product, caulosapogenin. Both these substances decompose at about 315°, and are sparingly soluble in alcohol, but dissolve readily in the latter when containing a little alkali hydroxide. When dissolved in acetic anhydride with a little chloroform, they give a rose-red coloration on the addition of a few drops of concentrated sulphuric acid. Caulophyllosapogenin, unlike caulosapogenin, does not yield a crystalline benzoyl derivative.

*Hexa-acetylcaulophyllosapogenin*, $C_{56}H_{82}O_9(CO{\cdot}CH_3)_6$. — This compound was prepared by heating caulophyllosapogenin for three hours with an excess of acetic anhydride, then removing the greater portion of the latter, and heating the residue with water in a current of steam. An amorphous solid was thus obtained, which melted at 160—162°. The substance was extremely soluble in the usual organic solvents, and could not be crystallised, but presumably was homogeneous. An analysis and a determination of its molecular weight gave the following results:

0·0978 gave 0·2517 $CO_2$ and 0·0795 $H_2O$. C=70·2; H=9·0.
0·9613, in 23·63 benzene, gave $\Delta t$ −0·180°. M.W.=1130.
$C_{68}H_{100}O_{15}$ requires C=70·6; H=8·7 per cent. M.W.=1156.

*Caulophyllosapogenin Dimethyl Ether*, $C_{56}H_{86}O_7(O{\cdot}CH_3)_2$.—In order to prepare this derivative, caulophyllosapogenin was dissolved in alcohol containing a little potassium hydroxide, and the solution heated with an excess of methyl iodide for several hours. The greater portion of the solvent was then removed, the mixture poured into dilute hydrochloric acid, and the resulting precipitate collected. When crystallised from dilute alcohol, it separated in stellate clusters of small needles, which melted at 240—242°:

0·0888 gave 0·2436 $CO_2$ and 0·0809 $H_2O$. C = 74·8; H = 10·1.

The number of methoxyl groups in the compound was determined by Perkin's modification of Zeisel's method:

0·1547 gave 0·0746 AgI. MeO = 6·4.

$C_{56}H_{86}O_7(O{\cdot}CH_3)_2$ requires C = 74·7; H = 9·9; MeO = 6·7 per cent.

*Caulophyllosapogenin dimethyl ether* is readily soluble in alcohol, ether, chloroform, or benzene. Its specific rotatory power was determined with the following result:

0·1222, made up to 20 c.c. with chloroform, gave $\alpha_D$ +0°32′ in a 2-dcm. tube, whence $[\alpha]_D$ +43·6°.

### *Identification of* l-*Arabinose, a Hydrolytic Product of Caulophyllosapogenin.*

The aqueous liquid obtained in the hydrolysis of caulophyllosapogenin, as above described, was exactly neutralised with sodium carbonate, and evaporated to dryness under diminished pressure. The residue was then digested with hot alcohol, the mixture filtered, and to the hot filtrate an equal volume of ethyl acetate was added, when a syrup was deposited. This was removed, and a further quantity of ethyl acetate added to the hot liquid. On keeping the latter for some time, a crystalline substance separated in small, hard nodules, which melted at 156°, and readily reduced Fehling's solution (Found, C = 39·9; H = 6·9. $C_5H_{10}O_5$ requires C = 40·0; H = 6·7 per cent.).

The optical rotatory power of the substance was determined with the following result:

0·1702, made up to 25 c.c. with water, gave $\alpha_D$ +1°27′ in a 2-dcm. tube, whence $[\alpha]_D$ +106·5°.

The substance yielded an osazone, which, when crystallised from dilute alcohol, was obtained in brownish-yellow needles, melting at 160° (Found, C = 62·2; H = 6·2. $C_{17}H_{20}O_3N_4$ requires C = 62·2; H = 6·1 per cent.).

From the above results it was evident that the sugar formed by the hydrolysis of caulophyllosaponin is a pentose, agreeing in all its properties with *l*-arabinose. In order further to confirm its identity, it was compared with a commercial specimen of arabinose. The latter melted at 156°, and when mixed with the above-described substance no depression in melting point was observed.

The glucoside caulophyllosaponin, $C_{66}H_{104}O_{17}$, is thus seen to be converted by hydrolysis into caulophyllosapogenin, $C_{56}H_{88}O_9$, and *l*-arabinose, $C_5H_{10}O_5$. A known quantity of the glucoside, when hydrolysed by dilute hydrochloric acid in the presence of alcohol, and the alcohol subsequently removed, yielded 72·6 per cent. of its weight of caulophyllosapogenin ($C_{66}H_{104}O_{17}$ requires $C_{56}H_{88}O_9 = 77·4$ per cent.). The hydrolysis of the glucoside is therefore to be represented by the following equation:

$$C_{66}H_{104}O_{17} + 2H_2O = C_{56}H_{88}O_9 + 2C_5H_{10}O_5.$$

### *Chloroform, Ethyl Acetate, and Alcohol Extracts of the Amorphous Material* (B).

*Chloroform Extract.*—This was a brittle, black solid, amounting to 10·5 grams. It was glucosidic in character, but no definite compound could be isolated from it.

*Ethyl Acetate Extract.*—This was a greyish-white solid, amounting to 24 grams. It was dissolved in hot alcohol, and the solution kept for some time, when a substance separated in needles, which decomposed at 250—255°. This substance was collected, and found to be identical with the previously described glucoside, caulosaponin, $C_{54}H_{88}O_{17}$ (Found, C = 64·0; H = 8·6. Calc., C = 64·3; H = 8·7 per cent.).

The alcoholic liquid remaining after the separation of the above glucoside was heated with dilute hydrochloric acid, when it yielded a small quantity of caulosapogenin, $C_{42}H_{66}O_6$, decomposing at 315°.

*Alcoholic Extract.*—This was a brittle, black solid, amounting to 12 grams. It was glucosidic in character, and yielded on hydrolysis a small quantity of caulosapogenin, $C_{42}H_{66}O_6$, which was identified by means of its benzoyl derivative, melting at 288°.

### *Summary and Physiological Tests.*

The material employed for this investigation consisted of the rhizome and roots of *Caulophyllum thalictroides* (Linné), Michaux.

A preliminary test showed the presence of an alkaloid, and a relatively small amount of an enzyme was obtained, which slowly hydrolysed amygdalin.

An alcoholic extract of the ground material, when distilled in a current of steam, yielded a small amount of a pale yellow essential oil. From the alcoholic extract, the following definite compounds were isolated: (i) A crystalline alkaloid, $C_{12}H_{16}ON_2$ (m. p. 137°;

$[\alpha]_D - 221 \cdot 6°$), which has been identified as methylcytisine; the *picrate* melts at 228°. (ii) A crystalline glucoside, *caulosaponin*, $C_{54}H_{88}O_{17},4H_2O$ (m. p. 250—255°), which yields a *deca-acetyl* derivative, $C_{54}H_{78}O_{17}(CO \cdot CH_3)_{10}$, melting at 135—140°, and on hydrolysis is resolved into *caulosapogenin*, $C_{42}H_{66}O_6$ (m. p. 315°), and dextrose. Caulosapogenin yields a *tetra-acetyl* derivative, $C_{42}H_{62}O_6(CO \cdot CH_3)_4$, melting at 120°, and a *diacetyl* derivative, $C_{42}H_{64}O_6(CO \cdot CH_3)_2$, melting at 160—162°, from which a crystalline *monosodio*-derivative, $C_{42}H_{63}O_6Na(CO \cdot CH_3)_2$, was prepared; it yielded, furthermore, a *tetrabenzoyl* derivative, $C_{42}H_{62}O_6(CO \cdot C_6H_5)_4$, melting at 288°, and a *monomethyl ether*, $C_{42}H_{65}O_5(O \cdot CH_3)$, which melts at 235°. (iii) A new crystalline glucoside, *caulophyllosaponin*, $C_{66}H_{104}O_{17}$ (m. p. 250—260°; $[\alpha]_D + 32 \cdot 3°$), which yields a *deca-acetyl* derivative, $C_{66}H_{94}O_{17}(CO \cdot CH_3)_{10}$, melting at 155—160°, and on hydrolysis is resolved into *caulophyllosapogenin*, $C_{56}H_{88}O_9$ (m. p. 315°), and arabinose. Caulophyllosapogenin yields a *hexa-acetyl* derivative, $C_{56}H_{82}O_9(CO \cdot CH_3)_6$, melting at 160—162°, and a *dimethyl ether*, $C_{56}H_{86}O_7(O \cdot CH_3)_2$, which melts at 240—242°, and has $[\alpha]_D + 43 \cdot 6°$. (iv) A phytosterol, $C_{27}H_{46}O$ (m. p. 153°). (v) Citrullol, $C_{28}H_{45}O_2(OH)_3$. (vi) A mixture of fatty acids, consisting of palmitic, stearic, cerotic, oleic and linolic acids. The alcoholic extract also contained a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 210°), and a comparatively small amount of resinous material.

The above-mentioned methylcytisine, $C_{12}H_{16}ON_2$, represents the alkaloid previously obtained by J. U. Lloyd (*Proc. Amer. Pharm. Assoc.*, 1893, **41**, 115), and designated "caulophylline," but he did not succeed in crystallising the base, and its composition was not determined. In view of its present identification, the name "caulophylline" should no longer be retained for this alkaloid.

The compound designated by the present authors as *caulosaponin*, $C_{54}H_{88}O_{17},4H_2O$, is undoubtedly identical with a crystalline glucoside first obtained by J. U. Lloyd ("Drugs and Medicines of North America," Vol. II, 1887, p. 151), and termed by him "leontin," although the formula deduced from its analysis was not correct. As it has now been completely characterised, it appears desirable that it should receive the new and distinctive name assigned to it.

For the purpose of determining the physiological action of methylcytisine and the two above-mentioned crystalline glucosides, caulosaponin and caulophyllosaponin, some tests were kindly conducted for us by Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, to whom our best thanks may here be expressed.

Methylcytisine has been found to be very similar in its action to cytisine, but not nearly so potent, the latter being at least ten times as active as the former on the blood pressure of the cat (compare Dale and Laidlaw, *J. Pharmacol. and Exp. Therap.*, 1912, **3**, 205). In other directions, such as the action on the ganglion cells supplying the eye and heart, methylcytisine is also very much weaker than cytisine. On the frog the difference in potency is not so obvious.

The glucosides, caulosaponin and caulophyllosaponin, showed the behaviour of the class of substances known as saponins. Solutions of these substances in physiological salt solution, although very dilute, were found to be powerfully hæmolytic for washed red blood corpuscles, and were also toxic for isolated, perfused frog's hearts. Whole blood and unwashed red blood corpuscles were unaffected, and both glucosides were without action on the frog's heart *in situ*. This difference in action on tissues in the body and on tissues freed from serum is known to be due to lipoid substances in the serum and tissues, for which substances saponins as a class have a marked affinity. The administration of the two glucosides by the mouth to small cats, in doses of 0·1 gram each, resulted in no symptoms of physiological activity other than a mild purgative action after several hours.

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# XXIV.—*Quercetagetin.*

## By ARTHUR GEORGE PERKIN.

QUERCETAGETIN was isolated from the flowers of the African marigold, *Tagetes patula*, by Latour and Magnier De La Source (*Bull. Soc. chim.*, 1877, [ii], **28**, 337), who state that it also occurs in other varieties of the same plant. In appearance and general properties it is described as resembling quercetin, the colouring matter of quercitron bark, and from this fact, together with its origin, the name *quercetagetin* is evidently derived. On the other hand, according to these authors, its crystalline form, solubility in 60 per cent. alcohol, and the numbers obtained on analysis (C=58·50; H=3·97) indicated that it was distinct from quercetin, $C_{27}H_{20}O_{12}$, and it was considered to possess the formula $C_{27}H_{22}O_{13}$ (anhydrous), or $C_{27}H_{22}O_{13},4H_2O$ (air-dried). In order to isolate the colouring matter from the flowers, boiling 85 per cent. alcohol was employed, and the deposit, which separated by partly evaporating the liquid, was freed from plant wax and other impurities by extraction with chloroform or carbon disulphide. The crude substance, dissolved in alcohol, was precipitated by water and crystallised from dilute alcohol. Some years ago my attention was directed to the subject by the late Prof. J. J. Hummel, who found that the flowers possessed well-defined tinctorial properties, and a preliminary examination was then carried out (see P., 1902, **18**, 75). As attempts to obtain an adequate supply of the flowers were not successful, the work was abandoned for a time, and it is only recently, owing to the kindness of Mr. T. H. Burkill, Reporter on Economic Products to the Government of India, and to Mr. D. Hooper, the Officiating Reporter, to whom I am indebted for several pounds of the petals, that a more complete investigation has been possible. The method adopted for the preparation of the quercetagetin has differed considerably from that employed by its discoverers, it having been recognised that the main quantity of the substance was not present in the free condition in the material, but as glucoside. On the other hand, for purposes of economy, no attempt was made to isolate the glucoside in the pure condition, this being reserved for subsequent investigation.

## EXPERIMENTAL.

The petals (1000 grams) were extracted for four hours with ten times their weight of alcohol, the extract evaporated to a small bulk, and poured into water, which caused the separation of viscous matter, possessing an aromatic odour. This was removed by shaking with ether (*A*), the brownish-yellow aqueous liquid diluted with water to 3500 c.c., and heated to boiling with the addition of 125 c.c. of 33 per cent. hydrochloric acid. On keeping, a small amount of yellow, crystalline substance usually separated, but as the main bulk of the desired compound remained dissolved, this could only be isolated by the tiresome operation of repeated extraction with much ether. After evaporation of the ether, a semi-crystalline, yellow residue remained, and this, by treatment with boiling water and keeping overnight, gave 17·2 grams of very crude colouring matter. It appeared evident from the method of isolation employed by Latour and Magnier De La Source that their product pre-existed in the flowers, for their operations did not involve the hydrolysis of a glucoside, and it was thus to be anticipated that some quantity of the substance was present in the ethereal extract (*A*). This proved to be the case, for by shaking the ether with dilute sodium carbonate solution, a yellow liquid was produced, which, when neutralised, gave a precipitate of 4·75 grams of the impure material. To expedite matters, at a later period some quantity of an alcoholic extract of the petals was very kindly prepared by Messrs. Hirst, Brooke, and Hirst, of Leeds, and in operating with this product it was stirred with boiling water, and the viscid, insoluble matter removed by decantation or by filtering through calico. The hydrolysis with hydrochloric acid was carried out at a much greater concentration than that given above, in the expectation that the colouring matter would now be deposited in bulk on cooling, so that the ether treatment could be avoided, but this hope was not realised.

For purification the crude colouring matter from 1000 grams of the petals (22 grams approx.) was treated with 130 c.c. of hot alcohol, filtered from a trace of a sparingly soluble substance (*B*), the filtrate diluted with 90 c.c. of boiling water, and the crystals which had separated overnight were collected and washed with dilute alcohol. The yield was 13·2 grams, or 1·3 per cent., from the petals, and could not be materially increased by working up the filtrate, as this mainly contained a resinous impurity. By recrystallisation from dilute alcohol, the product was now sufficiently pure for most purposes, but for complete purification it was necessary to prepare the acetyl derivative, and after recrystallisation to hydrolyse this with hydrochloric acid in the usual manner. Traces of a substance which formed a more soluble acetyl compound were thus removed, but a loss of some 25 per cent. of material hereby occurred. For analysis, the colouring matter was dried at 160°:

Found, C = 56·64, 56·47; H = 3·46, 3·31.

*$C_{15}H_{10}O_8$ requires C = 56·60; H = 3·14 per cent.

As deposited from dilute acetic acid or dilute alcohol, it contains water of crystallisation:

Found, $H_2O$ = 10·10.

$C_{15}H_{10}O_8,2H_2O$ requires $H_2O$ = 10·16 per cent.

Quercetagetin forms pale yellow, glistening needles or leaflets, closely resembling quercetin in appearance, readily soluble in hot alcohol, and very sparingly so in boiling water. It melts at about 318°, but owing to the darkening of the tube it was difficult to be certain to one degree. Very dilute alkali dissolves it with a pure yellow colour, which by air-oxidation becomes olive, and finally deep brown, but these changes are not so marked when a stronger alkali (10 per cent.) is employed. Alcoholic ferric chloride produces an olive-green coloration, whereas cold alcoholic lead acetate forms an orange-red precipitate, which, on keeping, becomes yellower, and finally develops a green tint. The yellow potassium salt precipitated by alcoholic potassium hydroxide rapidly changes to green, and ultimately assumes a brownish-black colour. Quercetagetin does not contain a methoxy-group, and beyond conversion into the hydriodide is unaltered by prolonged digestion with hydriodic acid.

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* The analyses given by Latour and Magnier De La Source (*loc. cit.*) indicate that their substance contained either a second colouring matter or some other impurity of higher carbon content.

Acetylquercetagetin is readily prepared by digesting quercetagetin with five times its weight of boiling acetic anhydride to which a few drops of pyridine have been added, for one hour. The solution diluted with its own volume of alcohol, on keeping, deposits crystals, which are purified by recrystallisation from a mixture of alcohol and acetic acid. For analysis, the substance (1 gram approx.) in 15 c.c. of acetic acid was hydrolysed by gradual addition of hydrochloric acid (15 c.c.) at the boiling point. Hot water was then added, and the crystals of quercetagetin, which separated on cooling, were collected, and dried at 160° (Found, $C_{15}H_{10}O_8=55·61$, 55·82. $C_{15}H_4O_8(C_2H_3O)_6$ requires $C_{15}H_{10}O_8=55·79$ per cent.).

Acetylquercetagetin consists of colourless needles, very sparingly soluble in alcohol. It melts at 209—211°, or slightly higher than was stated previously (203—205°, *loc. cit.*).

*Quercetagetin Sulphate.*—Quercetagetin closely resembles in general properties the colouring matters of the flavone group, and readily yields crystalline oxonium compounds when treated with mineral acids in the presence of acetic acid. Of these, only the sulphate, which is deposited in fine orange-coloured needles, was submitted to analysis (Found, $C=43·28$, 42·69; $H=3·29$, 3·26. $C_{15}H_{10}O_8,H_2SO_4$ requires $C=43·26$; $H=2·88$ per cent.). By treatment with water, it is converted into quercetagetin and sulphuric acid.

Monopotassium quercetagetin, $C_{15}H_9O_8K$ (Found, $K=10·74$), separates as an orange-yellow, semi-crystalline precipitate when potassium acetate is added to a solution of quercetagetin in hot absolute alcohol. It possesses the general characteristics of the monosubstituted flavonol salts, and is readily decomposed by boiling water with separation of quercetagetin.

*Action of Fused Alkalis on Quercetagetin.*—Five grams of quercetagetin were heated with 50 grams of potassium hydroxide and a little water to 200—220° for half an hour. The product was dissolved in water, the solution neutralised with acid, repeatedly extracted with ether, the extract evaporated, and the dark-coloured viscous residue, which partly solidified on keeping, treated with a little water. When no further separation occurred, the crystals were collected, drained on a tile, and purified by recrystallisation from water. The colourless needles melted at 194—196°, and possessed the properties of protocatechuic acid.

From the mother liquors no definite phenolic compound could be isolated, and a second alkali fusion at a slightly lower temperature was also fruitless in this respect. As a result of the later experiments described below, there can, however, be no doubt that such a compound is in reality produced during some stage of the hydrolysis, but is subsequently decomposed, probably by oxidation. Although it appeared likely that at a much lower temperature, with weaker alkali and exclusion of air, the desired result might be obtained, it has not been possible to spare sufficient of the rare material for this experiment.

*Quercetagetin Pentamethyl Ether*, $C_{20}H_{20}O_8$.—Quercetagetin (8 grams) dissolved in methyl alcohol (100 c.c.) was treated with excess of methyl iodide (50 c.c.), the mixture boiled, and a solution of potassium hydroxide (16 grams) in methyl alcohol added, drop by drop, during fourteen hours, this procedure being adopted as in the case of myricetin (T., 1902, **81**, 245) with the object of preventing an oxidation which readily occurs in the presence of the alkali. After removal of the unattacked methyl iodide and the greater portion of the alcohol by distillation, the residue was treated with ether, and the solution washed with water. By now shaking with dilute alkali, a dull yellow extract was obtained, which, on acidification, yielded a semi-crystalline precipitate. The residual ethereal liquid (*B*) was reserved for subsequent examination. The product was collected and purified by crystallisation from alcohol:

Found, $C=61{\cdot}93,\ 61{\cdot}85$; $H=5{\cdot}58,\ 5{\cdot}34$; $CH_3=19{\cdot}40$.
$C_{15}H_5O_3(O{\cdot}CH_3)_5$ requires $C=61{\cdot}86$; $H=5{\cdot}15$; $CH_3=19{\cdot}33$ per cent.

It consisted of pale yellow needles, melting at 161—162°, sparingly soluble in cold alcohol, and insoluble in cold alkaline solutions. If, however, to the pentamethyl ether suspended in dilute potassium hydroxide solution a little alcohol is added, the crystals now readily dissolve on shaking with the production of a yellow liquid, and the isolation of this compound in the manner above described was evidently due to the occurrence of some alcohol in the ether. Boiling concentrated potassium hydroxide solution also dissolves this compound, and on cooling, the potassium salt separates as a yellow, colloidal precipitate. With sulphuric acid, quercetagetin pentamethyl ether forms a yellow liquid, which is reddened by the addition of nitric acid.

*Acetylquercetagetin pentamethyl ether* crystallises from acetic anhydride in colourless needles, melting at 161—163°, and its solution in alcohol possesses a faint blue fluorescence.

*Quercetagetin Hexamethyl Ether*, $C_{21}H_{22}O_8$.—The ethereal liquid (*B*), containing that portion of the methylation product undissolved by dilute alkali, was evaporated, and the viscous residue treated with a little methyl alcohol. On keeping overnight, the crystals, which had then separated, were collected and recrystallised from the same solvent. The pale yellow product melted indefinitely between 130° and 140°, and as experiment indicated it to be a mixture of the pentamethyl ether with a second substance, to remove the former it was repeatedly crystallised from dilute alcoholic potassium hydroxide. In this manner, colourless, prismatic needles eventually separated, which melted at 141—143°, and appeared to be pure, but by recrystallisation from acetone the melting point rose to 157—158°:

Found, $C=62·74$; $H=5·50$; $CH_3=22·22$.

$C_{15}H_4O_2(O{\cdot}CH_3)_6$ requires $C=62·68$; $H=5·47$; $CH_3=22·38$ per cent.

The compound forms colourless needles, sparingly soluble in cold alcohol. The yield was extremely poor, although a considerable excess of alkali and iodide had been employed for the methylation, an indication that by this method it can only be produced with difficulty.

As it was desirable to prepare, if possible, some quantity of this hexamethyl ether, experiments were carried out on the action of methyl sulphate on the dry potassium salt of the pentamethyl compound, such a method having given good results in the case of quercetin (Waliaschko, *Arch. Pharm.*, 1904, **242**, 242) and myricetin (*loc. cit.*). 0·8 Gram of quercetagetin pentamethyl ether was added to a solution of 0·5 gram of potassium hydroxide in a little alcohol, the mixture evaporated to dryness, ground with 1·25 grams of methyl sulphate, and, after remaining overnight, treated with a further quantity of the sulphate. At the end of the second day, the product was washed with ether, digested with boiling water, and crystallised from dilute alcoholic potassium hydroxide. The colourless, prismatic needles melted at 141—142°, but after recrystallisation from acetone at 157—158°, and consisted of quercetagetin hexamethyl ether, which, it thus seems probable, may be dimorphous. The yield (0·2 gram) was, however, again poor, and this could only be accounted for by the fact that the salt of pentamethyl ether, being soluble in alcohol, suffers hydrolysis during the evaporation of the solution to dryness. On the other hand, the salts of the corresponding quercetin and myricetin compounds are insoluble and not so readily attacked in this manner.

*Quercetagetin Hexaethyl Ether*, $C_{27}H_{34}O_8$.—It has been shown, in the case of myricetin (*loc. cit.*), and more recently with quercetin and other flavone colouring matters (P., 1912, **28**, 328), that by the employment of excess of ethyl iodide and alkali, no difficulty is experienced in obtaining from these compounds good yields of their fully ethylated derivatives. A similar method was accordingly applied to quercetagetin, in the hope that a better result would be given than was the case with the methylation process. Ten grams of quercetagetin in 140 c.c. of alcohol were treated with 60 c.c. of ethyl iodide, and to the boiling mixture a concentrated solution of 24 grams of potassium hydroxide in alcohol was added, drop by drop, during two days. After removal of the unchanged ethyl iodide and the greater portion of the alcohol, the residual liquid was poured into ether, the solution washed with water, then with dilute alkali, and evaporated. The almost colourless, crystalline product, which melted at 135—137°, was dissolved in hot alcohol, a few drops of alcoholic potassium hydroxide were added, and the crystals, which separated on cooling, were collected. The pale yellow tint of the filtrate indicated the presence of a trace of the potassium salt of the pentaethyl compound. When obtained in this way, the substance was usually pure, and melted at 139—141°, but a second treatment was sometimes necessary. The yield was 6·35 grams:

Found, C = 66·44; H = 7·43; Et = 35·47.

$C_{15}H_4O_2(OEt)_6$ requires C = 66·66; H = 7·00; Et = 35·80 per cent.

*Quercetagetin hexaethyl ether* forms colourless needles, sparingly soluble in cold alcohol. With mineral acids in the presence of boiling acetic acid, it readily yields oxonium compounds, the sulphate separating in orange needles, whereas the crystals of the hydrochloride possessed a somewhat more yellow colour. This behaviour is analogous to that of quercetin pentamethyl ether (Watson, P., 1911, **27**, 163).

*Hydrolysis of Quercetagetin Hexaethyl Ether.*—If quercetagetin were in reality a flavonol derivative, the gentle hydrolysis of its hexaethyl derivative, by means of alcoholic potassium hydroxide, should, as has been previously shown to be the case with quercetin (Herzig, *Ber.*, 1909, **42**, 155) and myricetin (*loc. cit.*), yield products affording proof of such a structure.

Five grams of the substance, dissolved in a hot solution of 10 grams of potassium hydroxide in 50 c.c. of 80 per cent. alcohol, were heated on the steam-bath for seven hours. The liquid, which did not solidify on keeping (distinction from quercetin and myricetin), was evaporated to dryness, the residue dissolved in water, and the solution saturated with carbon dioxide. An oily product (*A*) thus separated, which was removed by ether, and weighed approximately 2·7 grams. The aqueous liquid, on acidification, gave a colourless, crystalline precipitate (*B*) (2·23 grams), and this was purified by recrystallisation (Found, C=62·55; H=7·04; Et=26·70. $C_6H_3(OEt)_2{\cdot}CO_2H$ requires C=62·85; H=6·66; Et=27·61 per cent.). It melted at 167—169°, and consisted of protocatechuic acid diethyl ether. The oily product (*A*), which only yielded crystals after keeping for some weeks, was drained on tile, and crystallised two or three times from minute amounts of methyl alcohol, the only solvent found suitable for the purpose, but in which it is somewhat readily soluble:

Found, C=61·22; H=7·75; Et=36·71.
$C_{16}H_{24}O_6$ requires C=61·53; H=7·69; Et=37·17 per cent.

This substance, for which the name of *quercetagetol tetraethyl ether* is suggested, consists of prismatic needles, melting at 46—48°, soluble, although not very readily, in dilute alkali, indicating the presence of a free hydroxyl group. With acetic anhydride in the usual manner, it gave an oily acetyl compound, which up to the present has not become crystalline.

As it was to be anticipated that this compound contained a carbonyl group and should thus yield an oxime, a mixture of 0·56 gram of the substance, 1 gram of anhydrous sodium acetate, and 0·25 gram of hydroxylamine hydrochloride was digested with 25 c.c. of boiling alcohol for four hours (compare Lapworth and Steele, T., 1911, **99**, 1884). After removal of the alcohol, the residue, on treatment with water, gave to ether an oily product, which on long keeping solidified, and was repeatedly crystallised from a mixture of light petroleum and carbon disulphide:

Found, C=58·74; $H_2O$ lost; N=4·38.
$C_{16}H_{25}O_6N$ requires C=58·71; N=4·28 per cent.

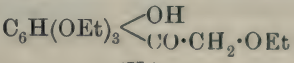
This *oxime* consists of colourless needles, melting at 93—95°.

With the object of obtaining further indication of the constitution of the quercetagetol tetraethyl ether, 1 gram, dissolved in 50 c.c. of 2 per cent. potassium hydroxide solution, was gradually treated with a cold solution of 3 grams of potassium permanganate in 50 c.c. of water. Oxidation readily took place, but towards the end of the operation the pink coloration very slowly disappeared. The mixture was filtered, the precipitated oxide exhausted with boiling water, the clear liquid when cold saturated with carbon dioxide, and extracted with ether to remove traces of unattacked substance (if present). From the aqueous solution after acidification, ether now removed a small amount of a crystalline acid, and this, when recrystallised from water, formed colourless, prismatic needles, melting at 100—102°, with the production of a clear liquid, which commenced to effervesce between 129° and 136°. Sufficient of this compound was unfortunately not available for analysis, but for purposes of future study, it will be referred to as *quercetagetinic acid.*

Quercetagetin hexaethyl ether thus yields by the above-described method of hydrolysis diethylprotocatechuic acid (I), and a ketone, quercetagetol tetraethyl ether, which there is little reason to doubt, in view of the previous study of quercetin pentaethyl ether and myricetin hexaethyl ether (*loc. cit.*), possesses the constitution (II):

$C_6H_3(OEt)_2{\cdot}CO_2H$

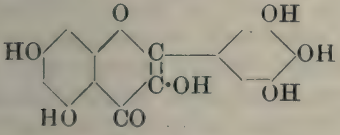
(I.)



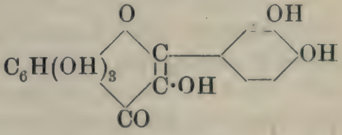
$C_6H(OEt)_3<^{OH}_{CO \cdot CH_2 \cdot OEt}$

(II.)

Quercetagetin is indeed, as its general reactions also indicate, a hexahydroxyflavonol isomeric with myricetin. It differs, however, from this colouring matter, and also from the closely allied quercetin in possessing a tetrahydroxybenzene in place of the phloroglucinol nucleus which they contain, as the following formulæ indicate:



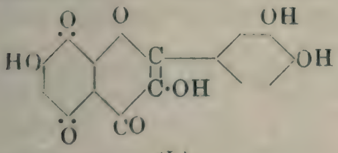
Myricetin.



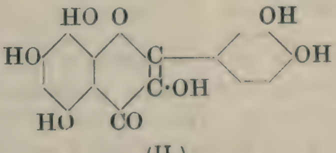
Quercetagetin.

With regard to the exact position of the hydroxyl groups in the tetrahydroxybenzene nucleus of quercetagetin, which could occupy the positions: O:OH:OH:OH·=1 : 2 : 3 : 4, 1 : 3 : 4 : 5, 1 : 2 : 3 : 5, or 1 : 2 : 4 : 5, the evidence is scanty, and may be especially difficult to ascertain in the case of so rare a colouring matter.

According to Nierenstein and Wheldale (*Ber.*, 1911, **44**, 3487), quercetin when oxidised by chromic acid gives the quinone, quercetone (I), which by reduction is converted into the flavonol (II):



(I.)

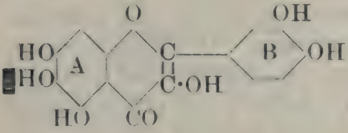


(II.)

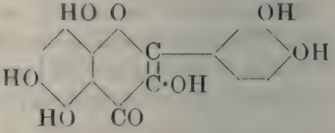
but as the latter compound melts at 352—359°, its methyl ether at 147—149°, sintering at 136—138°, and the acetyl compound could not be crystallised, it cannot therefore be quercetagetin.

On the other hand, the fact that quercetagetin pentamethyl ether is insoluble in alkali suggests that in this compound the unmethylated hydroxyl group occupies the position (5) and is adjacent to the carbonyl group, although this again cannot yet be regarded as certain because, whereas quercetagetin yields, although with difficulty, a hexamethyl derivative, no fully methylated flavonol compound possessing an hydroxyl group in this position has previously been obtained by the employment of methyl iodide and alkali. It is to be noted, however, that in almost every instance of this group hitherto studied a phloroglucinol nucleus has been present in the substances which it is quite reasonable to suppose might exert an influence in this respect not possessed by a tetrahydroxybenzene group.

From a consideration of these points, it thus appears likely that quercetagetin is to be represented by one or other of the following formulæ:



(I.)



(II.)

Of these the second seems, at first sight, most probable, because should quercetagetin possess the pyrogallol grouping present in I, a more rapid oxidation of the substance in alkaline solution, with accompanying colour change, as in the case of myricetin, would be expected.

*Dyeing Properties.*—As is to be anticipated from its constitution quercetagetin readily dyes mordanted fabrics shades of a generally similar character to those given by other well-known flavonol colouring matters. A comparison of the dyeings given by this compound and quercetin on mordanted woollen cloth are, however, interesting, in that colours yielded by the former possess a distinctly yellower character.

| | Chromium. | Aluminium. | Tin. | Iron. |
|---|---|---|---|---|
| Quercetagetin | Dull olive-yellow | Yellow-orange | Brown | Brownish-black |
| Quercetin...... | Orange-yellow | Bright orange | Reddish-brown | Olive-black |

This result is somewhat remarkable in that it has been previously shown that fisetin (trihydroxy-), quercetin (tetrahydroxy-), and myricetin (pentahydroxy-flavonol) yield practically identical colours, unless the duller and yellower shades given by quercetagetin are ascribed to slight oxidation during the dyeing process. This, however, does not appear to be the case, for when chalk is employed during the operation no marked change of shade is observed, as is the case when dyeing with gossypetin (T., 1899, **75**, 828). An important point in this respect is that quercetagetin, whatever tetrahydroxybenzene group it may contain, possesses attached respectively to the nuclei *A* and *B* pairs of ortho-hydroxyl groups, each of which is capable of inducing a strong tinctorial effect with mordants. With a compound of this constitution, containing as it does only a single chromophore, according to the quinonoid theory only one of these pairs can influence the dyeing operation, although it is to be conceived that the quinonoid arrangement might vary in distinct lake particles. Thus, whereas it appears certain and has been discussed in former communications that in quercetin the shades are mainly the result of the effect of the orthohydroxyl groups in its catechol nucleus (*B*), it is probable, on the other hand, that the yellow colours given by quercetagetin are governed by the hydroxyl groups present in the nucleus (*A*).

The more sparingly soluble colouring matter from the flowers, which was present in the crude quercetagetin to the extent of about 1 per cent., resembled rhamnetin (quercetin monomethyl ether) in appearance, but was not, as seemed probable, a methyl ether of quercetagetin, for hydriodic acid indicated the absence of a methoxy-group. When crystallised from alcohol, it forms somewhat indefinite groups of minute needles, and dissolves in alkaline solutions with an orange colour, passing to green on dilution with water. Owing to the minute amount available, no further examination of this compound was attempted.

*Dyeing Properties of the Flowers.*—Employing mordanted woollen cloth, the following shades were obtained:

| Chromium. | Aluminium, | Tin. | Iron. |
|---|---|---|---|
| Yellowish-brown | Pale dull yellow | Deep yellow-orange | Brownish-black |

These possessed a somewhat redder character than those given by quercitron bark, and were similar to, although not so red as, those from patent bark. In this case the tinctorial effect is mainly due to glucoside.

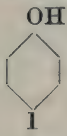
Further work with quercetagetin will be carried out as soon as opportunity occurs, and an investigation of the isomeric and closely allied colouring matter gossypetin is in progress, the results of which it is anticipated will throw further light on the exact structure of both compounds.

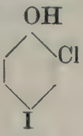
Clothworkers' Research Laboratory,
The University, Leeds.

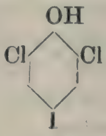
# XXV.—*The Chlorination of Iodophenols. Part II. The Chlorination of* o-*Haloid Derivatives of* p-*Iodophenol.*

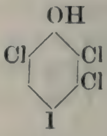
By George King, M.Sc. (Priestley Research Scholar of the University of Birmingham), and Hamilton McCombie.

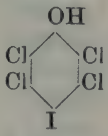
It has been shown by Brazier and McCombie (T., 1912, **101**, 968) that *p*-iodophenol (I), when treated with chlorine in a cold carbon tetrachloride solution, yielded an unstable dichloride, which decomposed rapidly, evolving hydrogen chloride and forming 2-chloro-4-iodophenol (II):


(I.)


(II.)


(III.)


(IV.)


(V.)

This iodophenol, in turn, when chlorinated, gave an unstable dichloride, which, on decomposition, yielded 2 : 6-dichloro-4-iodophenol (III). This phenol was converted, by successive stages, into 2 : 3 : 6-trichloro- (IV) and 2 : 3 : 5 : 6-tetrachloro-4-iodophenol (V).

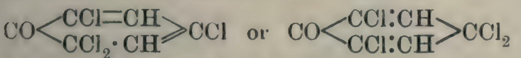
In contradistinction to the phenols, the acyl derivatives yielded relatively stable iodo-dichlorides. The iodo-dichlorides of all the benzoyl derivatives were found to remain perfectly stable for months, whilst those of the acetyl derivatives could be kept for several days before any decomposition took place.

The work has now been extended to a study of various derivatives of *p*-iodophenol, in which one or both of the ortho-positions relative to the hydroxyl group are occupied by halogen atoms.

The first compound studied was 2 : 4 : 6-tri-iodophenol (VI). Willgerodt (*Ber.*, 1892, **25**, 3495) states that 2 : 4 : 6-tri-iodophenol, when chlorinated in chloroform solution, gave an oily substance, and seems to have been under the impression that, both in this case and in the case of *o*-iodophenol, chlorination results in the displacement of iodine in the molecule by chlorine. The authors have found, however, that, when pure tri-iodophenol is chlorinated in a dilute carbon tetrachloride solution, a dichloride could be isolated. This dichloride, although unstable, was much more stable than those derived from *p*-iodophenol and its chloro-substitution products, and differed further from these compounds in that, on decomposition, chlorine was eliminated and tri-iodophenol was regenerated.

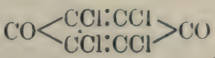
The relative stability of the dichlorides of the acyl derivatives of *p*-iodophenol finds its parallel also in the case of tri-iodophenol. The acetyl derivatives of tri-iodophenol yielded, on chlorination, a dichloride, which decomposed only after being kept in a sealed tube for six weeks exposed to sunlight. The dichloride of the benzoyl derivative has remained stable for a period of twelve months.

Since, in the present research, the dichloride of tri-iodophenol has been obtained when employing solutions in carbon tetrachloride, whilst Willgerodt, by using chloroform as solvent, obtained a product in which iodine was substituted by chlorine, it seemed probable, when considering the stability of the dichloride, that the effect of the solvent had to be taken into consideration, and accordingly a study of the influence of the solvent on the chlorination has been made. It has been found that, by the use of a suitable solvent, a dichloride of tri-iodophenol could be obtained, whilst, by employing other media for chlorination, displacement of iodine by chlorine took place. Among the solvents employed, it was found that chlorination in carbon tetrachloride and in light petroleum yielded the dichloride, whilst in ether, in chloroform, and in glacial acetic acid, gave rise to products in which the iodine was replaced by chlorine. In the latter group of solvents, the influence of glacial acetic acid was fully investigated, and it was found that four distinct substances were obtained, namely: (1) a red, oily substance, constituting about 1 per cent.; (2) tetrachloro*cyclo*hexadienone (VII), constituting about 90 per cent.; (3) chloroanil (VIII), about 6 per cent.; (4) a colourless substance, melting at 110°, and containing 66 per cent. of chlorine.



$\mathrm{CO}{<}\begin{matrix}\mathrm{CCl{=}CH}\\ \mathrm{CCl_2\cdot CH}\end{matrix}{>}\mathrm{CCl}$ or $\mathrm{CO}{<}\begin{matrix}\mathrm{CCl{:}CH}\\ \mathrm{CCl{:}CH}\end{matrix}{>}\mathrm{CCl_2}$

(VII.)



$\mathrm{CO}{<}\begin{matrix}\mathrm{CCl{:}CCl}\\ \mathrm{CCl{:}CCl}\end{matrix}{>}\mathrm{CO}$

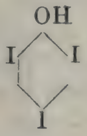
(VIII.)

Brazier and McCombie (*loc. cit.*, p. 977) identified traces of chloroanil as one of the products which result when chlorine acts on *p*-iodophenol in carbon tetrachloride at 50—60°. It has also been noticed by the authors that small quantities of chloroanil are produced when 2:4-di-iodophenol is chlorinated. In the case of tri-iodophenol, a copious yield of chloroanil was obtained when chlorination took place in boiling acetic acid solution, and it is interesting to note that a similar displacement of bromine by chlorine has been observed in glacial acetic acid solution (Benedikt and Schmidt, *Monatsh.*, 1883, **4**, 604).

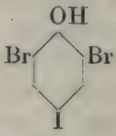
Hence, in considering the action of chlorine on tri-iodophenol, it is to be noted that both the solvent and the temperature have a marked influence on the products.

The interesting fact that, although the dichloride of *p*-iodophenol decomposed with evolution of hydrogen chloride and the formation of chloroiodophenol, the dichloride of tri-iodophenol gave off chlorine with regeneration of tri-iodophenol, led the authors to examine the behaviour of other *p*-iodophenols, in which the positions 2 and 6 are occupied by halogen atoms. Brazier and McCombie have shown that both 2-chloro-4-iodophenol (II) and 2 : 6-dichloro-4-iodophenol (III) yield unstable iodo-dichlorides, which decompose with evolution of hydrogen chloride.

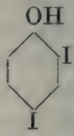
In the first place, the authors examined the behaviour towards chlorine of 2 : 6-dibromo-4-iodophenol (IX), which was easily prepared by means of the diazo-reaction from the corresponding amino-compound. This compound yields an iodo-dichloride, the stability of which was very similar to that of the tri-iodo-compound, also, on decomposition, chlorine was evolved, and the original dibromoiodophenol was regenerated. Thus it is seen that, with two iodine or with two bromine atoms in the 2 : 6-position of *p*-iodophenol, the iodo-dichlorides decompose with evolution of chlorine, whilst, if there are two chlorine atoms in these positions, hydrogen chloride is evolved, and ring substitution takes place. In some way or another, the two bromine and two iodine atoms are able to protect the hydrogen atoms in position 3 and 5 from attack by the chlorine resulting from the decomposition of the iodo-dichloride.



(VI.)



(IX.)

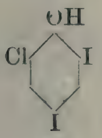


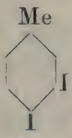
(X.)

The next compound which was examined was 2 : 4-di-iodophenol (X). This substance, on treatment with chlorine, yielded an iodo-dichloride which was more unstable than the corresponding compound derived from tri-iodophenol, but was very similar, in its behaviour, to the dichloride derived from *p*-iodophenol. Like that compound, it decomposed with evolution of hydrogen chloride, and the formation of a chloroiodophenol. The product was 6-chloro-2 : 4-di-iodophenol (XI); the proof of this constitution was furnished by the conversion of the decomposition product, by means of nitric acid, into 6-chloro-2 : 4-dinitrophenol. This compound has been described by various investigators, and its constitution is undoubted (compare Griess, *Annalen*, 1859, **109**, 286; Faust and Müller, *ibid.*, 1874, **173**, 312; Faust and Saame, *Annalen Suppl.*, 1869–70, **7**, 195; Seifart, *ibid.*, 197; Brazier and McCombie, *loc cit.*).

Di-iodophenyl acetate yields an iodo-dichloride, which is less stable than the corresponding tri-iodo-derivative, for, whilst the latter remained stable for six weeks, the former, under similar conditions, decomposed in ten days. When the dichloride of di-iodophenyl acetate did decompose, hydrogen chloride was given off, whilst in the case of the tri-iodo-compound, chlorine was evolved. The benzoyl derivative of di-iodophenol yielded a very stable iodo-dichloride, behaving in that respect similarly to the benzoyl derivatives of all the *p*-iodophenols which have been studied.

In this study of the chlorination of di-iodophenol, and of tri-iodophenol, and their simple acyl derivatives, it has always been found, by naalysis, that only one of the iodine atoms becomes multivalent. Since it has been shown by Willgerodt and Desaga (*Ber.*, 1904, **37**, 1301) that *m*-di-iodobenzene unites with chlorine in two stages to form the compounds $C_6H_4I \cdot ICl_2$ and $C_6H_4(ICl_2)_2$, it seems as if the hydroxyl group in these polyiodo-phenols exerted a protective influence over one or more of the iodine atoms. The influence thus exerted by the hydroxyl and the acyl groups is similar to that of the methyl group, observed by Willgerodt and Simonis (*Ber.*, 1906, **39**, 269), who state that 3 : 4-di-iodotoluene (XII) yields only a mono-iodo-dichloride. Another instance of the destruction of the tervalency of an iodine atom is furnished by the behaviour of 3 : 5-di-iodonitrobenzene (XIII). Willgerodt and Ernst (*Ber.*, 1901, **34**, 3406) were able to prepare only a mono-iodo-dichloride from this compound, the negative nitro-group having destroyed the tervalency of one of the iodine atoms in the same way as the positive methyl group did in 3 : 4-di-iodotoluene.


(XI.)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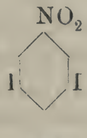
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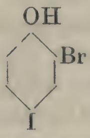
(XIV.)

The last derivative of *p*-iodophenol which was studied was 2-bromo-4-iodophenol (XIV). This compound, on chlorination, was found to behave in the same way as did 2 : 4-di-iodophenol, 2-chloro-4-iodophenol, and 2 : 6-dichloro-4-iodophenol. Hydrogen chloride was evolved, and 6-chloro-2-bromo-4-iodophenol was produced.

In considering the stability of the iodo-dichlorides described in this paper, it is to be noticed that various factors exert different influences. In the preparation of the iodo-dichlorides, it is found that, if the chlorine is not very dry, either the iodo-dichloride is not formed, or, if it is formed, it is unstable. Again, if the iodo-dichlorides are placed in sealed tubes, they are found to decompose much more rapidly than if they are left exposed to the air. The effect of light on the decomposition was studied, but this was found to have practically no influence. The stability is also influenced very largely by the purity of the iodo-dichloride, the effect of impurities on the stability being markedly less when substitution of chlorine in the nucleus takes place. Provided very pure products were chlorinated, and the iodo-dichloride after being separated was washed thoroughly with carbon tetrachloride and dried rapidly on a porous plate, it was found possible to determine the melting points of these compounds with a fair degree of accuracy. In this manner the following melting points, not elsewhere recorded, have been determined: *p*-iodophenol dichloride, 63—64°; 2-chloro-4-iodophenol dichloride, 62—64°; 2: 6-dichloro-4-iodophenol dichloride, 58—60°.

The preparation of 2: 4: 6-tri-iodophenol has been described by Körner (*Annalen*, 1866, **137**, 213), Messinger and Vortmann (*Ber.*, 1889, **22**, 2313), Brenans (*Compt. rend.*, 1901, **132**, 831), and Carrasco (*Boll. chim. farm.*, 1908, **47**, 109). After an extended investigation of the various methods, it was found most satisfactory to work according to the equation:

$$C_6H_5\cdot OH + 2KOH + 3I_2 = C_6H_2I_3\cdot OH + 3KI + 3H_2O.$$

The production of tri-iodophenol depends on the amount of potassium hydroxide present, and the yield is good when a large excess of potassium hydroxide is employed, since the potassium salt is formed directly. This method, however, is not an economical one, since all the potassium iodide is lost. In the presence of a moderate excess of potassium hydroxide, the main product is not tri-iodophenol, but the red tetraiodo-diphenylenequinone (compare Lautemann, *Annalen*, 1861, **120**, 309; Wilkie, *J. Soc. Chem. Ind.*, 1911, **30**, 398; 1912, **31**, 208).

## EXPERIMENTAL.

The method used for the continuous preparation of 2: 4: 6-tri-iodophenol was as follows. To 600 c.c. of an 8 per cent. potassium iodide solution containing 38·1 grams of iodine, 3·1 grams of phenol dissolved in 20 c.c. of water were added, 5·6 grams of potassium hydroxide in 150 c.c. of water were poured slowly down the sides of the flask, and the solution was shaken thoroughly. After remaining for not more than three hours, the precipitate was collected, and the filtrate, containing excess of iodine and potassium iodide, was reserved for a second preparation. (For subsequent preparations, 25 grams of iodine were dissolved in the filtrate, and the same quantities of phenol and potassium hydroxide as above were added.) The precipitate was dissolved in potassium hydroxide, and the tri-iodophenol reprecipitated with 30 per cent. hydrochloric acid, when it was obtained in a granular condition, and free from the red quinone which often accompanies it. By fractional precipitation from methylated spirit by the addition of water up to a dilution of 40 per cent., 10 to 12 grams of tri-iodophenol, melting at 155—156°, were obtained.

### *Action of Chlorine on* 2 : 4 : 6-*Tri-iodophenol: Influence of the Solvent and the Temperature.*

This chlorination was carried out in different solvents, and under different conditions of temperature.

*In Carbon Tetrachloride Solution.*—Chlorine was bubbled slowly through an ice-cold 0·7 per cent. solution of the tri-iodophenol in carbon tetrachloride, and the yellow precipitate which appeared was separated. The precipitate was found to possess all the properties of an iodo-dichloride, and melted and decomposed at 55—60°. After a short time, the compound decomposed slowly, chlorine and some hydrogen chloride being evolved. The mass resulting from the decomposition contained free iodine, but when recrystallised from a mixture of methyl alcohol and water, gave pure tri-iodophenol.

In order to study the influence of temperature on this chlorination, chlorine was led into a 20 per cent. solution of tri-iodophenol in carbon tetrachloride at 50°. Much iodine was liberated, and when the passage of chlorine was continued, a dark red powder was precipitated. This product was rich in iodine and chlorine, and completely volatile; it was most probably iodine monochloride.

The solution, on concentration, yielded a yellow oil, which was soluble in dilute potassium hydroxide, and, although not an iodo-dichloride, contained a large amount of chlorine, which had probably displaced some or all of the iodine atoms.

*In Chloroform and Ether.*—Even from an ice-cold 20 per cent. solution of tri-iodophenol in these solvents, no iodo-dichloride could be isolated; only an oily substance was obtained (compare above, and Willgerodt, *Ber.*, 1892, **25**, 3494).

*In Light Petroleum.*—The iodo-dichloride was obtained when light petroleum was used as solvent.

*In Glacial Acetic Acid.*—A slow stream of chlorine was bubbled through a solution of tri-iodophenol in glacial acetic acid at 15°. After from six to eight minutes,* when the solution had darkened considerably with liberated iodine, cold water was added, when a light yellow mass was precipitated. This precipitate consisted of: (1) A red, oily substance, forming about 1 per cent. of the precipitate; (2) tetrachloro*cyclo*hexadienone (VII), constituting about 90 per cent. of the precipitate; (3) chloroanil, about 6 per cent.; (4) a colourless substance, which melted at 110°, and contained 66 per cent. of chlorine.

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* It was noticed repeatedly that if water were added after one minute, a red substance was precipitated; this was stable in air, and contained no free iodine. Methyl alcohol changed the mass to pale yellow, the alcohol remaining colourless.

The separation of these four substances was effected by means of methyl alcohol, which retained the oily compound in solution, whilst the chloroanil and the colourless substance crystallised out from the solution. By the addition of water to the filtrate, the tetrachloro*cyclo*hexadienone was precipitated, and when crystallised from a mixture of methyl alcohol and water, separated in very long, pale yellow needles, melting at 121—122°. This was identical with the compound obtained by Zincke (*Ber.*, 1894, **27**, 545) (Found, Cl = 61·02. Calc., Cl = 61·7 per cent.).

Although chlorination of tri-iodophenol in cold acetic acid gave a small yield of chloroanil, a theoretical yield of this substance was obtained by passing a rapid stream of chlorine for three hours through a boiling concentrated solution. It was sparingly soluble in the acetic acid, and, on cooling, crystallised in large, flat plates, which, when recrystallised from benzene, separated in long, yellow needles, melting at 285° (Found, Cl = 57·2. Calc., Cl = 57·7 per cent.).

In attempting to determine the nature of this compound, a small quantity was treated with phenylhydrazine in absolute alcohol. Much nitrogen was evolved, and the substance obtained, when crystallised from a mixture of methyl alcohol and water, separated in pale brown needles, melting at 229—230°, and containing 55·4 per cent. of chlorine. A similar reaction has been noticed by Purgotti (*Gazzetta*, 1894, **24**, 554) when chloroanil is treated with hydrazine hydrate, but both these reactions require further investigation.

### 2 : 4 : 6-*Tri-iodophenyl Acetate*, $C_6H_2I_3 \cdot OAc$.

Tri-iodophenol was acetylated by the action of acetic anhydride in the presence of a drop of sulphuric acid (compare Orton and Smith, T., 1908, **93**, 1247). When crystallised from benzene, chloroform, or glacial acetic acid, it separated in long needles, melting at 153°.

The *dichloride* was prepared in carbon tetrachloride solution, and formed as a yellow incrustation, which melted and decomposed at 144—147°. For analysis, a specimen was prepared from the pure acetyl derivative, and was washed thoroughly with carbon tetrachloride:

0·1743 gave 0·2981 AgCl + AgI.

$C_8H_5O_2I_3$ requires AgCl + AgI = 0·2956.

A small quantity of this iodo-dichloride was sealed up and exposed to sunlight. After six weeks it slowly decomposed with the liberation of a little iodine. The product, when crystallised from a mixture of methyl alcohol and water, consisted of tri-iodophenyl acetate.

### 2 : 4 : 6-*Tri-iodophenyl Benzoate*, $C_6H_2I_3{\cdot}OBz$.

Since some difficulty was experienced in preparing this compound by the Schotten-Baumann reaction (compare Brazier and McCombie, *loc. cit.*, p. 970), benzoylation in pyridine was employed. The product, when crystallised from acetone, separated in large, transparent plates, melting at 137° (Found, I = 66·01. Calc., I = 66·15 per cent.).

The *dichloride* was obtained from carbon tetrachloride solution as a yellow incrustation, which melted and decomposed at 132—134°.

0·0946 gave 0·1419 AgCl + AgI.

$C_{12}H_7O_2Cl_2I_3$ requires AgCl + AgBr = 0·1451.

This iodo-dichloride has remained stable for a period of twelve months. On treating the compound with 10 per cent. potassium hydroxide, no iodoso-compound was formed, but the benzoyl derivative was regenerated.

### 2 : 6-*Dibromo-4-iodophenol*, $C_6H_2Br_2I{\cdot}OH$ (IX).

2 : 6-Dibromo-4-aminophenol, obtained by the bromination of *p*-nitrophenol and subsequent reduction with tin and hydrochloric acid (Möhlau, *Annalen*, 1895, **289**, 95), was converted into the corresponding iodophenol by means of the diazo-reaction. 2 : 6-Dibromo-4-iodophenol is moderately volatile in steam, and can be separated by this means from the mixture after diazotisation and the addition of potassium iodide. When crystallised from light petroleum, or from a mixture of methyl alcohol and water, it separates in long, transparent needles, melting at 105°:

0·0972 gave 0·1546 AgBr + AgI.

$C_6H_3OBr_2I$ requires AgBr + AgI = 0·1571.

The *dichloride* was prepared in a 20 per cent. carbon tetrachloride solution, and separated, when chlorine had been passed through the solution for three hours, in bright yellow needles, melting at 63°:

0·0666 gave 0·1306 AgCl + AgBr + AgI.

$C_6H_3OCl_2Br_2I$ requires AgCl + AgBr + AgI = 0·1332.

The whole of the chlorine in this iodo-dichloride was shown to be attached to the multivalent iodine atom by estimating the iodine liberated when the iodo-dichloride in methyl-alcoholic solution reacted with potassium iodide. Titration with sodium thiosulphate gave Cl = 14·92.

$C_6H_3OCl_2Br_2I$ requires Cl = 15·5 per cent.

The dibromo-iodophenol, precipitated during the titration, was identified and weighed.

This iodo-dichloride was found to remain stable during three days, but then gradually decomposed with liberation of chlorine. Examination of the decomposition product showed it to be dibromo-iodophenol.

### 2 : 6-*Dibromo-4-iodophenyl Acetate*, $C_6H_2Br_2I\cdot OAc$.

This compound was obtained by acetylation in presence of a drop of sulphuric acid. When crystallised from a mixture of methyl alcohol and water, it separated in long, colourless needles, melting at 87°:

0·0974 gave 0·1410 AgBr + AgI.

$C_8H_5O_2Br_2I$ requires AgBr + AgI = 0·1419.

The *dichloride* was exceptionally difficult to obtain, and was precipitated only after passing chlorine for two days through a concentrated carbon tetrachloride solution. It consisted of stable, bright yellow, feathery needles, which melted and decomposed at 116—117°:

0·0312 gave 0·0567 AgCl + AgBr + AgI.

$C_8H_5O_2Cl_2Br_2I$ requires AgCl + AgBr + AgI = 0·0571.

### 2 : 6-*Dibromo-4-iodophenyl Benzoate*, $C_6H_2Br_2I\cdot OBz$.

This compound was prepared by the pyridine method, and when crystallised from the mixture of methyl alcohol and water, separated in short, colourless, prismatic needles, melting at 97°:

0·0486 gave 0·0623 AgBr + AgI.

$C_{13}H_7O_2Br_2I$ requires AgBr + AgI = 0·0616.

The *dichloride*, obtained by chlorinating for half an hour, was a stable, granular, yellow powder, melting and decomposing at 123—125°:

0·0501 gave 0·0806 AgCl + AgBr + AgI.

$C_{13}H_7O_2Cl_2Br_2I$ requires AgCl + AgBr + AgI = 0·0814.

### *Dichloride of* 2 : 4-*Di-iodophenyl Acetate*, $Cl_2I\cdot C_6H_3\cdot OAc$.

This substance was obtained as a pale yellow, granular precipitate when chlorine was led into a 20 per cent. solution of 2 : 4-di-iodophenyl acetate in carbon tetrachloride. It melted and decomposed at 127—130°:

0·1124 gave 0·1871 AgCl + AgI.

$C_8H_6O_2Cl_2I_2$ requires AgCl + AgI = 0·1858.

After remaining in a sealed tube for ten days without undergoing any visible change, this iodo-dichloride decomposed, spontaneously generating a considerable pressure of hydrogen chloride.

### 2 : 4-*Di-iodophenyl Benzoate*, $C_6H_3I_2\cdot OBz$.

This derivative was prepared by the action of 1 gram of benzoyl chloride on 1·5 grams of di-iodophenol dissolved in 4 c.c. of pyridine. On pouring the solution into dilute sulphuric acid, the benzoate was precipitated, and when crystallised from methyl alcohol or from light petroleum, separated in needles, melting at 98° (Found, I = 56·3. Calc., I = 56·44 per cent.).

The *dichloride* was obtained as a very pale yellow, granular powder, melting and decomposing at 134—135°:

0·1034 gave 0·1501 AgCl + AgI.

$C_{13}H_8O_2Cl_2I_2$ requires AgCl + AgI = 0·1503.

This iodo-dichloride, like that of tri-iodophenyl benzoate, was exceptionally stable, and has remained so for over six months. Attempts to prepare the iodoso-compound regenerated the benzoyl derivative.

### *Action of Chlorine on* 2 : 4-*Di-iodophenol : Preparation of* 6-*Chloro*-2 : 4-*di-iodophenol*, $C_6H_3OClI_2$.

The di-iodophenol required for these experiments was prepared from *p*-iodophenol according to the method described by Neumann (*Annalen*, 1887, **241**, 79).

A slow stream of chlorine was passed through an ice-cold solution of 10 grams of di-iodophenol in 300 c.c. of carbon tetrachloride, resulting in the precipitation of 11 grams of an orange-yellow iodo-dichloride, which melted and decomposed at 59—61°. Precipitation was complete in five to ten minutes, and the separated solid was quickly transferred to a flat dish cooled in ice. Energetic decomposition took place immediately, hydrogen chloride being evolved and some iodine liberated. When the iodine had volatilised, there remained a light brown, semi-solid mass, weighing 2·5 grams. Since recrystallisation yielded only oily products, the decomposition product obtained from several chlorinations was treated with sodium hydrogen sulphite and distilled in a current of steam. If steam was passed slowly through the mixture, a solid product was obtained. This substance, after several recrystallisations from light petroleum, separated in colourless needles, melting at 99°. The yield was 22 per cent. of the theoretical:

0·1262 gave 0·2014 AgCl + AgI.

$C_6H_3OClI_2$ requires AgCl + AgI = 0·2030.

The mixed haloids were oxidised with potassium dichromate and sulphuric acid, chlorine was liberated, and the silver iodate formed was reduced with sulphurous acid (compare McNair, T., 1893, **63**, 1052), but this method was found to give results for iodine 1 to 2 per cent. too low:

Found, I = 65·24.

$C_6H_3OClI_2$ requires I = 66·74 per cent.

The constitution of this chlorodi-iodophenol was determined by heating the compound with concentrated nitric acid in the presence of a few drops of sulphuric acid. Much iodine was liberated, and on pouring into sodium hydrogen sulphite solution and extracting with ether, 6-chloro-2:4-dinitrophenol, melting at 112°, was obtained.

On chlorinating 6-chloro-2:4-di-iodophenol, an iodo-dichloride was obtained in slender, pale yellow plates, melting and decomposing at 50°. After some time, the compound decomposed with liberation of hydrogen chloride. Owing, however, to the poor yields which were obtained, this decomposition was not followed any further.

### 6-*Chloro*-2:4-*di-iodophenyl Acetate*, $C_6H_2ClI_2 \cdot OAc$.

When prepared by means of acetic anhydride and sulphuric acid, this compound was obtained in theoretical yield, and, after three crystallisations from a mixture of methyl alcohol and water, separated in colourless needles, melting at 74—75°:

0·0872 gave 0·1274 AgCl + AgI.

$C_8H_5O_2ClI$ requires AgCl + AgI = 0·1267.

Estimation of the iodine by oxidation of the mixed haloids gave I = 58·7. Calc., I = 60·1 per cent.

The *dichloride* consisted of pale yellow, feathery needles, melting and decomposing at 110°:

0·0807 gave 0·1467 AgCl + AgI.

$C_8H_5O_2Cl_3I$ requires AgCl + AgI = 0·1472.

After being kept in a sealed tube for three and a-half days, this iodo-dichloride decomposed rapidly, with evolution of hydrogen chloride. Attempts to prepare the iodoso-compound failed, chloroiodophenyl acetate being regenerated.

### 6-*Chloro*-2 : 4-*di-iodophenyl Benzoate*, $C_6H_2ClI_2 \cdot OBz$.

This compound was prepared by both the pyridine and the Schotten-Baumann method. In both cases a product was obtained, which, after long keeping, solidified partly, and melted at about 92°, but could not be crystallised.

The *dichloride* was a yellow, granular powder, which melted and decomposed at 117—119°:

0·0432 gave 0·0680 AgCl + AgI.

$C_{13}H_7O_2Cl_3I_2$ requires AgCl + AgI = 0·0700.

Attempts to regenerate the benzoate from the iodo-dichloride gave only oily products.

### 2-*Bromo*-4-*iodophenol*, $C_6H_3BrI \cdot OH$.

*o*-Bromophenol was nitrated, and the mixture of nitro-compounds (4-nitro- and 6-nitro-) was separated by steam distillation. 2-Bromo-4-nitrophenol, on reduction, gave the amino-compound which by means of the diazo-reaction yielded 2-bromo-4-iodophenol, which was obtained from the mixture by distillation in a current of steam.

2-*Bromo*-4-*iodophenol* is very soluble in all ordinary organic solvents, but is only sparingly so in water, crystallising from it in long, colourless needles; crystallisation from light petroleum gave short, white, prismatic needles, melting at 51°:

0·1081 gave 0·1504 AgBr + AgI.

$C_6H_4OBrI$ requires AgBr + AgI = 0·1529.

### 2-*Bromo*-4-*iodophenyl Acetate*, $C_6H_3BrI \cdot OAc$.

This compound is very soluble in methyl and ethyl alcohols, but crystallises from light petroleum in clusters of ill-defined, rectangular plates, melting at 52°:

0·0909 gave 0·1142 AgBr + AgI.

$C_8H_6O_2BrI$ requires AgBr + AgI = 0·1127.

The *dichloride* was obtained only after continuous chlorination for six hours. It forms a golden-yellow incrustation, which melts and decomposes at 113°:

0·0353 gave 0·0623 AgCl + AgBr + AgI.

$C_8H_6O_2Cl_2BrI$ requires AgCl + AgBr + AgI = 0·0608.

### *Action of Chlorine on 2-Bromo-4-iodophenol: Preparation of 6-Chloro-2-bromo-4-iodophenol*, $C_6H_2ClBrI{\cdot}OH$.

2-Bromo-4-iodophenol was chlorinated in 20 per cent. carbon tetrachloride solution for forty minutes, when the iodo-dichloride was precipitated in bright yellow needles, melting and decomposing at 69—70°. After washing with carbon tetrachloride, the iodo-dichloride was found to remain stable for about forty-five minutes. Rapid decomposition then took place, sufficient heat being evolved to melt the decomposition product. The free iodine liberated during the decomposition was removed, and the product was purified by solution in alcohol and precipitation with water. The substance is very soluble in alcohol and most other organic solvents, but crystallised slowly from light petroleum. By seeding with the product thus obtained, crystallisation was effected from a mixture of methyl alcohol and water, when the substance separated in colourless needles, melting at 81—82°:

0·0322 gave 0·0542 $AgCl + AgBr + AgI$.

$C_6H_3OClBrI$ requires $AgCl + AgBr + AgI = 0{\cdot}0547$.

On further chlorination of 6-chloro-2-bromo-4-iodophenol, the *dichloride* separated in bright yellow, feathery needles, melting and decomposing at 66—67°. After remaining at room temperature for two hours, this iodo-dichloride darkened and became oily; hydrogen chloride was evolved in the decomposition.

Attempts were made to prepare the acetyl derivative of 6-chloro-2-bromo-4-iodophenol, but it could not be crystallised satisfactorily. The iodo-chloride separated as a pale yellow, granular precipitate, melting and decomposing at 102—103°.

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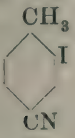
## XXVI.—2 : 2′-*Ditolyl*-5 : 5′-*dicarboxylic Acid.*

By JAMES KENNER and ERNEST WITHAM.

IN connexion with investigations on 2 : 2′-ditolyl (Kenner and Turner, T., 1911, **99**, 2101; Kenner, P., 1912, **28**, 187), it was decided to attempt the preparation of nuclear-substituted derivatives of this substance. The present paper contains an account of the synthesis of 2 : 2′-ditolyl-5 : 5′-dicarboxylic acid, and certain of its derivatives, from those of *o*-iodo-*p*-toluic acid by treatment with copper powder according to Ullmann's well-known process.

The iodotoluic acid just mentioned has already been described by Kloeppel (*Ber.*, 1893, **26**, 1733), who obtained it from the corresponding amino-derivative, but as it was desired to examine the behaviour of its nitrile towards copper powder, the latter substance (I) was first prepared from *o*-amino-*p*-toluonitrile, described by Banse (*Ber.*, 1894, **27**, 2163) and Borsche (*Ber.*, 1903, **36**, 4359). This compound, and the methyl and ethyl esters of the carboxylic acid obtained by its hydrolysis, were then heated with copper powder, and respectively converted into 5 : 5′-dicyano-2 : 2′-ditolyl (II), diethyl 2 : 2′-ditolyl-5 : 5′-dicarboxylate (III), and the corresponding dimethyl ester:



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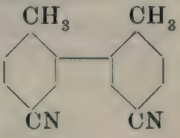

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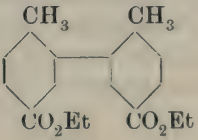

(III.)

It may be remarked that the preparation of the 5 : 5′-dicyano-derivative is the first instance in which Ullmann's method has been applied to an iodonitrile, and it was found that the success of the operation in this case, and, indeed, in the other two cases now described, required careful attention to the conditions of the experiment. In each case the iodo-derivative must be heated to the requisite temperature as rapidly as possible, and the duration of the treatment with copper powder should not be extended beyond a certain length of time, which varies with the substance. Prolonged heating leads to the formation of tarry products, from which the desired compound cannot be isolated. It has also been the invariable experience of one of us that tarry products of high boiling point result in the preparation of 2 : 2′-ditolyl, for which somewhat prolonged heating is prescribed by Ullmann. The formation of such by-products probably occurs to a greater or less extent in all reactions of this type, and is presumably due to secondary reactions, in which the excess of copper powder used in the condensation plays the part of a catalyst.*

When the experiments now described were well advanced, a paper appeared (*Ber.*, 1912, **45**, 1187) in which Liebermann described the results of his investigation of the action of oxalyl chloride on derivatives of diphenyl in the presence of aluminium chloride. In the case of 2 : 2′-ditolyl, the sole product isolated was a dicarboxylic acid, to which the constitution of a 5 : 5′-dicarboxylic acid was provisionally assigned. The properties of the acid (m. p. 287°) and of its dimethyl ester (m. p. 124°) do not, however, agree with those of our synthetical products, which respectively melt above 300° and at 134°, and we were therefore disinclined to accept Liebermann's formula. To reassure ourselves on this point, dimethyl iodoterephthalate (IV) was converted by treatment with copper powder into tetramethyl diphenyl-2 : 5 : 2′ : 5′-tetracarboxylate (V), in order that a comparison might be instituted with the tetramethyl ester prepared by Liebermann from the oxidation product of his ditolyldicarboxylic acid.

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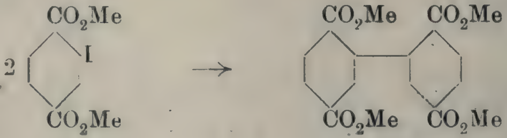
* The presence of small amounts of moisture and fat in the "Naturkupfer-C" used in our experiments (compare Schlenk, Mair, and Bornhardt, *Ber.*, 1911, **44**, 1172, footnote; and Schmidlin, *Ber.*, 1912, **45**, 3176, footnote) may conceivably be partly responsible for the formation of tarry matter, but the explanation suggested above appears to us to be more probable. For examples of the catalytic action of copper, see, *inter alia*, Knoevenagel and Heckel, *Ber.*, 1903, **36**, 2823; Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, [viii], **4**, 347; *Compt. rend.*, 1901, **132**, 1333; Ullmann, *Ber.*, 1905, **38**, 729, 2120, 2211; Ipatiev, *Ber.*, 1909, **42**, 2089, 2098; 1910, **43**, 3387.



(IV.) (V.)

In this case, also, the synthetical product melted considerably higher than Liebermann's compound, and, leaving out of account the possibility of an isomerism of the type recently observed by Cain, Coulthard, and Micklethwait (T., 1912, **101**, 2298), it would appear that the series of compounds isolated by Liebermann must have a different constitution from that originally attributed to them.

The remaining possibilities (assuming a symmetrical structure) are that the carboxyl groups may be in the 3 : 3′-, the 4 : 4′-, or the 6 : 6′-positions. The first of these is excluded by the non-identity of the tetramethyl ester (m. p. 141°) of the tetracarboxylic acid, obtained by oxidation, with the synthetical tetramethyl diphenyl-2 : 3 : 2′ : 3′-tetracarboxylate (m. p. 161°), recently described by one of us (P., 1912, **28**, 277). The second possibility is rejected by Liebermann, whilst the properties of the synthetical 2 : 2′-ditolyl-6 : 6′-dicarboxylic acid, described by Mayer (*Ber.*, 1911, **44**, 2303), together with the absence of any 4 : 5-dimethylphenanthraquinone from the products of the reaction, show that this formula is also untenable. Liebermann's compound would appear, therefore, to possess an unsymmetrical structure, and this suggestion derives support from the fact that the acid obtained, together with 2 : 7-dimethylphenanthraquinone, by the action of oxalyl chloride on 4 : 4′-ditolyl, is considered by Liebermann also to be unsymmetrical.*

## EXPERIMENTAL.

### o-*Iodo*-p-*toluonitrile*, $C_6H_3MeI{\cdot}CN$.

A solution of 45 grams of *o*-amino-*p*-toluonitrile in 900 c.c. of 10 per cent. sulphuric acid was cooled to 0°, and diazotised with a solution of 23 grams of sodium nitrite in 60 c.c. of water. On the gradual addition of a solution of 80 grams of potassium iodide in 140 c.c. water, the iodo-compound rapidly separated and solidified. It was washed with hot sulphurous acid solution and hot dilute sodium hydroxide solution, and then crystallised from ethyl acetate. The yield was 60 per cent. of the calculated. The compound may also be crystallised from light petroleum (b. p. 90—110°), but this solvent is less effective in removing small amounts of a red compound (probably azotoluonitrile), which accompanies the main product.

o-*Iodo*-p-*toluonitrile* forms magnificent colourless, rhombic crystals, melting at 57·5°, and is readily soluble in ether, chloroform, or hot alcohol:

0·3526 gave 0·3433 AgI. I = 52·6.

$C_8H_6NI$ requires I = 52·26 per cent.

*o*-Iodo-*p*-toluic acid, $C_6H_3MeI{\cdot}CO_2H$, resulted when the above nitrile was boiled for three and a-half hours with 10 parts of 15 per cent. sodium hydroxide solution, and the solution, after cooling and dilution, was acidified. The acid, after crystallisation from alcohol, melted at 205—206°, and agreed in its properties with those described by Kloeppel (*Ber.*, 1893, **26**, 1734) (Found, C = 36·64; H = 2·62. M.W. = 263. Calc., C = 36·64; H = 2·67 per cent. M.W. = 262). Its barium, ferric, cobalt, and lead salts are sparingly, its calcium salt moderately, soluble in hot water, whilst its magnesium salt is readily soluble.

The *methyl* ester, prepared by esterification with sulphuric acid, boils at 194°/52 mm., and slowly solidifies to a mass of crystals, melting at 28°:

0·3254 gave 0·4676 $CO_2$ and 0·0998 $H_2O$. C = 39·16; H = 3·41.
0·2827 ,, 0·2423 AgI. I = 45·83.

$C_9H_9O_2I$ requires C = 39·13; H = 3·26; I = 46·01 per cent.

---

* In view of this result, tetramethyl diphenyl-3 : 4 : 3′ : 4′-tetracarboxylate has recently been prepared in this laboratory by Miss A. M. Mathews, B.Sc., from dimethyl 4-iodophthalate, and as its properties were found to correspond with those of the product obtained by Liebermann in his experiments with 3 : 3′-ditolyl, the symmetrical structure assigned by him in this case appears to be confirmed.—J. K.

The *ethyl* ester, prepared in a similar manner, boils at 242°/175 mm.:

0·3482 gave 0·5288 $CO_2$ and 0·1174 $H_2O$. C=41·42; H=3·75.
0·3460 ,, 0·2801 AgI. I=43·75.

$C_{10}H_{11}O_2I$ requires C=41·38; H=3·83; I=43·79 per cent.

The *amide* crystallises from alcohol in leaflets, melting at 167°:

0·1590 gave 7·8 c.c. $N_2$ at 20° and 722 mm. N=5·45.

$C_8H_8ONI$ requires N=5·37 per cent.

The *hydrazide* crystallises from alcohol in prisms, melting at 151°. It is readily soluble in chloroform, but sparingly so in ether or light petroleum:

0·1618 gave 14·6 c.c. $N_2$ at 16° and 733 mm. N=10·33.

$C_8H_9ON_2I$ requires N=10·02 per cent.

5 : 5′-*Dicyano*-2 : 2′-*ditolyl*, $CN\cdot C_6H_3Me\cdot C_6H_3Me\cdot CN$, was prepared by rapidly heating *o*-iodo-*p*-toluonitrile to 260°, and adding an equal weight of copper powder in portions at intervals during ten minutes. The temperature was maintained at 260° for fifteen minutes longer, during which time the mixture was kept well stirred, and the product was then cooled and extracted with benzene. After concentration, light petroleum (b. p. 90—110°) was added until no more oily matter was precipitated, and the almost colourless solution was then allowed to crystallise by spontaneous evaporation. The nitrile was further purified by crystallisation from ethyl acetate, and was thus obtained in leaflets, melting at 159°. The yield of pure material was small. The compound was readily soluble in chloroform, ether, or hot alcohol, but only sparingly so in light petroleum:

0·1400 gave 0·4235 $CO_2$ and 0·0670 $H_2O$. C=82·50; H=5·32.
0·1570 ,, 16·8 c.c. $N_2$ at 15° and 739 mm. N=12·39.

$C_{16}H_{12}N_2$ requires C=82·71; H=5·17; N=12·07 per cent.

2 : 2′-*Ditolyl*-5 : 5′-*dicarboxylic acid*,

$CO_2H\cdot C_6H_3Me\cdot C_6H_3Me\cdot CO_2H$,

readily resulted on hydrolysis of its esters with alcoholic potassium hydroxide. It is only moderately soluble in alcohol, and separates from this solvent in a microcrystalline condition. Its melting point lies above 300°:

0·1230 gave 0·3182 $CO_2$ and 0·0590 $H_2O$. C=71·3; H=5·3.
0·1324 required 9·7 c.c. *N*/10-NaOH. M.W.=273

$C_{16}H_{14}O_4$ requires C=71·11; H=5·2 per cent. M.W.=270.

Its barium, calcium, cobalt, and mercuric salts, as well as those of the alkali metals, are soluble in water, whilst the ferric and lead salts are only sparingly soluble.

The *dimethyl* ester was prepared by gradual addition, in the space of twenty minutes, of copper powder to an equal weight of methyl *o*-iodo-*p*-toluate at 260°, and heating the mixture further for half an hour. After cooling, the product was extracted with ether, and the crude product thus obtained amounted to 65 per cent. of the calculated quantity. It was further purified by crystallisation from light petroleum (b. p. 60—80°), and finally from methyl alcohol. It forms prisms, melting at 133° :

0·1450 gave 0·3844 $CO_2$ and 0·0786 $H_2O$. C = 72·3 ; H = 6·02.

$C_{18}H_{18}O_4$ requires C = 72·48 ; H = 6·04 per cent.

The *diethyl* ester, prepared in a similar manner, was separated from the copper powder by extraction with ether, and after crystallisation the crude product was drained on porous earthenware. The yield was 55 per cent. of the calculated. It was further purified by crystallisation from light petroleum (b. p. 40—60°), in which medium it is readily soluble, and was thus obtained in small prisms, melting at 76° :

0·1288 gave 0·3474 $CO_2$ and 0·0765 $H_2O$. C = 73·4 ; H = 6·59.

$C_{20}H_{22}O_4$ requires C = 73·62 ; H = 6·75 per cent.

### *Tetramethyl Diphenyl-*2 : 5 : 2′ : 5′*-tetracarboxylate*, $C_6H_3(CO_2Me)_2\cdot C_6H_3(CO_2Me)_2$.

Dimethyl iodoterephthalate was required for the synthesis of this compound, and was prepared by saturating a suspension of 20 grams of iodoterephthalic acid in 200 c.c. of cold methyl alcohol with hydrogen chloride, and finally warming the mixture on the water-bath until complete solution had taken place. The pure ester, melting at 80°, separated on cooling, and a further quantity was obtained from the mother liquor. Abbes (*Ber.*, 1893, **26**, 2952) gives the melting point as 77—78°.

The addition of copper powder to this ester at 260° was followed by a vigorous reaction and a rise in temperature to 310°. After an equal weight of copper powder had been gradually added to the ester in the course of twenty minutes, the mixture was heated for a further forty-five minutes. After cooling, the mass was extracted with hot benzene, from which tetramethyl diphenyltetracarboxylate separated in the pure condition. It forms small prisms, melting at 156°. The yield amounted to 70 per cent. of that calculated, and would probably have been greater still if precautions had been taken in view of the tendency to sublimation exhibited by this compound :

0·1410 gave 0·3208 $CO_2$ and 0·0616 $H_2O$. C = 62·45 ; H = 4·85.

$C_{20}H_{18}O_4$ requires C = 62·18 ; H = 4·85 per cent.

The ester was easily hydrolysed by alcoholic potassium hydroxide, and the acid was isolated in the usual manner.

*Diphenyl*-2 : 5 : 2′ : 5′-*tetracarboxylic acid* melts above 300°, and is remarkable for its very sparing solubility in the usual solvents, in contrast with the ready solubility of its isomerides. It reacts, however, with cold sodium hydrogen carbonate solution. For analysis it was dried at 180°:

0·1562 gave 0·3304 $CO_2$ and 0·0464 $H_2O$. C = 57·69; H = 3·30.
0·1070 required 12·87 c.c. $N/10$-NaOH. M.W. = 332·6.
$C_{16}H_{10}O_8$ requires C = 58·18; H = 3·03 per cent. M.W. = 330.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed the greater part of the cost of this investigation.

THE UNIVERSITY,
SHEFFIELD.

# XXVII.—*The Action of Ammonia and Alkylamines on Reducing Sugars.*

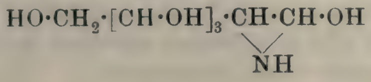
By JAMES COLQUHOUN IRVINE, ROBERT FRASER THOMSON, M.A., B.Sc., and CHARLES SCOTT GARRETT, B.Sc.

THE abundant literature which has accumulated on the action of alkalis on carbohydrates is an index of the importance attached to such inquiries, and shows that attention has been specially directed to the reaction between ammonia and the reducing sugars. This is particularly the case since the discovery of the amino-sugar, glucosamine, and many researches were apparently based on attempts to produce compounds of this type by simple condensation.

Considering the views at present held regarding the constitution both of reducing sugars and of glucosamine, it is not surprising that in no case has the latter compound been obtained by the direct action of ammonia on a hexose. The products actually formed are frequently complex. In some instances definite additive compounds seem to be produced, but generally condensation proceeds through loss of a molecule of water, and the ultimate production of the so-called "imines" of the sugars.

As the constitution generally assigned to compounds of this type seemed to us to be inconsistent with the results obtained in this laboratory on the condensation of sugars and amino-compounds, we considered it advisable to re-investigate the problem. In particular the constitution of glucoseimine is a question of some importance in view of the isomerism of the compound with glucosamine, and in throwing light on the structure of the analogous arabinoseimine from which Fischer prepared glucosaminic acid (*Ber.*, 1902, **35**, 3787) as one of the steps in the synthesis of glucosamine.

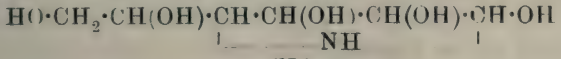
Lobry de Bruyn, who first isolated glucoseimine (*Ber.*, 1895, **28**, 3082), ascribed to the compound the following structure:



$$\mathrm{HO{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}\underbrace{CH{\cdot}CH}_{NH}{\cdot}OH}$$

(I.)

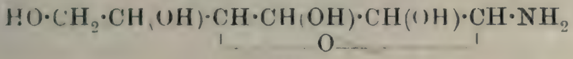
This was subsequently modified by Wohl, who holds that an imino-group connects the $\gamma$-carbon atoms:



$$\mathrm{HO{\cdot}CH_2{\cdot}CH(OH){\cdot}\underbrace{CH{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH}_{NH}{\cdot}OH}$$

(II.)

On the other hand, the formula for arabinoseimine which best explains the relationship between this compound and glucosaminic acid is one in which an amino-group is directly attached to the terminal carbon atom of the chain, and this leads to a third alternative formula for glucoseimine:



$$\mathrm{HO{\cdot}CH_2{\cdot}CH(OH){\cdot}\underbrace{CH{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH}_{O}{\cdot}NH_2}$$

(III.)

The remaining possibility, which represents the compound as an imino-glucose, is derived from the hypothetical aldehyde ammonia compound by loss of a molecule of water:

$$\mathrm{HO{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH{:}NH}$$

(IV.)

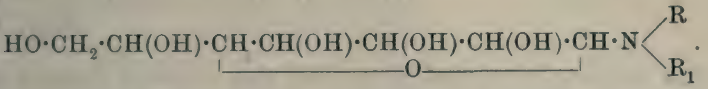
We have endeavoured to discriminate between these four alternatives, and, although all the results obtained are not entirely consistent, the bulk of the evidence points to formula III as being the most suitable. The two imino-ring formulæ are rejected on the ground that ammonia is without action on alcoholic solutions of sucrose or of $\alpha$-methylglucoside. Negative evidence of a more conclusive nature was afforded by the fact that tetramethyl-$\alpha$-methylglucoside is similarly unaffected by the action of alcoholic ammonia. In this case all the hydroxy-positions in the parent sugar are substituted, and only the oxygen atom of the ring is available for condensation. Even in the case of such a highly reactive compound as gluconolactone, we find that the action of ammonia gives rise to gluconamide, and no cyclic nitrogen derivatives were formed. The collective evidence of these results shows that the condensation under discussion is confined to the reducing group of the free sugar

This limits the alternatives to formulæ III and IV, either of which might result from the dehydration of an aldehyde ammonia derivative. No positive evidence, however, exists of the formation of additive compounds of this type from glucose, as Stone's results have been called in question by Lobry de Bruyn.

On account of the ease with which glucoseimine is hydrolysed, it is difficult to obtain satisfactory evidence of the presence of the amino-group. Nitrogen is certainly evolved on the addition of nitrous acid, but this is doubtless preceded by the removal of a molecule of ammonia from the compound. The reducing action, and the absence of the property of salt formation, which is so characteristic of glucosamine, we have now shown to be due to the same cause. Further consideration of all four formulæ indicates that the compound ought either to exhibit mutarotation or to exist in two stereoisomeric forms which are not spontaneously interconvertible. The detection of mutarotation in solution is thus, in this particular instance, of little value in distinguishing between formulæ III and IV, but the fact that we have observed this phenomenon is in accordance with the former alternative, as it brings the compound into line with glucoseanilide and other similar derivatives. Our observations of mutarotation were, however, not very decisive, owing to the instability of the compound and the speed with which equilibrium is attained, or a combination of these factors.

Attempts to prepare glucoseimine synthetically from specific $\alpha$- and $\beta$-derivatives of glucose led to a curious result. The action of ammonia in ethereal solution on $\alpha$- and $\beta$-penta-acetylglucoses gave in each case acetamide, and the imino-biose described by Sjollema (*Rec. trav. chim.*, 1899, **18**, 292). Considering the conditions adopted in these experiments, which were carried out in the cold, it is evident that the action of the ammonia is not confined to hydrolysis of the acetyl groups and subsequent reaction with the unsubstituted sugar. The imino-biose is, in fact, only formed when glucoseimine is heated, and, moreover, free glucose could not have been formed in the reaction as it is quite insoluble in ether. The imino-biose must therefore have resulted from the loss of one molecule of ammonia from two molecules of tetra-acetylglucoseimine, and the acetyl groups were only removed in the final stage of the reaction. Similarly, the action of ammonia on tetra-acetylbromoglucose also gave rise to the imino-biose, together with acetamide and ammonium bromide. This result is also significant as an index that the amino-group in glucoseimine occupies the glucosidic position in the sugar residue.

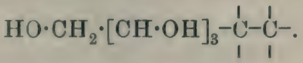
The evidence thus obtained in favour of formula III was supplemented by the study of the behaviour of glucose towards alkylamines. Only on the analogy of this formula should condensation of the sugar with secondary amines take place. We find that glucose reacts with difficulty with ethylamine, diethylamine, and dimethylamine, giving, in the first-mentioned case, a crystalline ethylaminoglucose which exhibits measurable mutarotation. These condensations thus give products of the following general type:



$$HO\cdot CH_2\cdot CH(OH)\cdot \underbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot N\Big\langle{}^{R}_{R_1}\ .$$

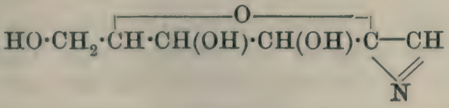
The action of ammonia on an alcoholic solution of fructose was also studied, as the results obtained by Lobry de Bruyn, in which he isolated the compound $C_{12}H_{20}O_8N_2$, did not seem to admit of any simple explanation. We have confirmed his results, and also added to the complexities involved in this reaction by the isolation of a second product, $C_6H_9O_4N$. This substance is quite inactive, but is nevertheless not a derivative of glutose, as it is converted into glucosephenylosazone displaying the normal activity. This points to extremely complex reactions resulting when nitrogen is introduced into the penultimate position in the ketose molecule. The change must here, as in many other cases when sugars are acted on by alkaline reagents, be accompanied by oxidation.

The constitution of the compound $C_6H_9O_4N$ is indicated by the fact, mentioned above, that it is converted into glucosephenylosazone, as this result suggests the presence of the grouping:

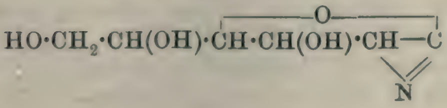


$$HO\cdot CH_2\cdot[CH\cdot OH]_3-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-.$$

It is, however, evident that the hydrogen and oxygen content demand a rearrangement to the corresponding γ-oxidic structure. Nitrogen must thus connect the two terminal carbon atoms, and two alternatives remain:

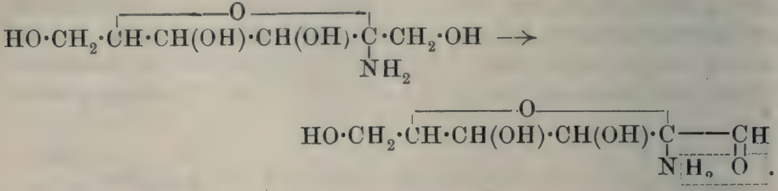


(I.)



(II.)

Between these alternatives we are unable to discriminate, but formula I is to be preferred, as the formation of the compound probably involves the following decomposition of the unknown fructoseimine:



$$HO\cdot CH_2\cdot \overbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot \underset{NH_2}{C}}^{O}\cdot CH_2\cdot OH \rightarrow HO\cdot CH_2\cdot \overbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot \underset{NH_2}{C}}^{O}-\underset{O}{CH}$$

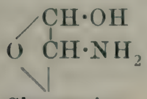
This view was supported by the fact that the same inactive compound was produced by the action of ammonia, in methyl-alcoholic solution, on glucosone. It will also be seen that the relationship between this compound and 2:5-ditetrahydroxybutylpyrazine, which is the main product of the action of ammonia on fructose, is a fairly simple one.

The most notable property of the compound, for which the name fructoseazine is suggested, is its stability towards acids. When heated with 2 per cent. aqueous hydrogen chloride for several hours, it remained quite unaltered, and, for this reason, we have discarded any alternative formula involving coupling of the hexose residues. The above behaviour is in sharp contrast to the ready hydrolysis of glucoseimine or the glucosealkylimines. The nitrogen is, however, easily expelled in the form of ammonia by the action of alkalis.

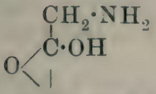
It is evident that the derivatives of sugars containing amino- or substituted amino-groups may be divided into two classes. In the one class, which includes glucosamine and *iso*glucosamine, the reducing group is unsubstituted, the compounds do not undergo hydrolytic changes when heated with acids, and thus possess the property of salt formation. In glucoseimine and the related compounds, nitrogen occupies the reducing position, and hydrolysis with acids takes place so readily that definite salts cannot be isolated.

This remarkable difference in stability seems to be due to the relative positions occupied by nitrogen with reference to the reducing group. Stable compounds are, in fact, only formed when nitrogen is linked to the carbon atom directly connected to the reducing group. Substitution of the reducing group, or of any hydroxyl group other than that adjacent to it, results in unstable products. The essential difference in structure shown by typical members of each of these two classes is shown below:

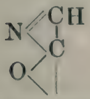
*Class A (Stable).*



Glucosamine.

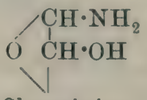


*iso*Glucosamine.

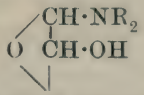


Fructoseazine.

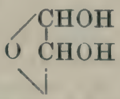
*Class B (Unstable).*



Glucoseimine.



Alkylaminoglucoses.



Fischer's aminoglucose.*

The simple structural difference between the types *A* and *B* seems at first sight insufficient to account for the great difference in properties. It must, however, be remembered, that the reducing group in sugars is distinctly acidic, and may thus combine with an amino-group, which is favourably situated, so as to form a second internal ring in the molecule. These conditions are realised in the case of glucosamine (Class *A*), for which we have previously, on perfectly independent grounds, suggested a ring structure (T., 1912, **101**, 1128), but are excluded in the compounds included under *B*, which must thus be regarded as open-chain amino- or substituted amino-glucoses.

The conclusions drawn above receive a certain amount of support by the fact that the aminoglucose corresponding with the amino-methylglucoside recently isolated by Fischer (*loc. cit.*) is, compared with the isomeric glucosamine, considerably less stable to acids. In this case, the reducing group of the sugar is unsubstituted, and the amino-group occupies the ε-position. Further, as already indicated, the compound $C_6H_9O_4N$, for which a ring structure containing nitrogen is now deduced, is perfectly stable when boiled with dilute acids.

## EXPERIMENTAL.

### *Mutarotation of Glucoseimine.*

The glucoseimine was prepared by the method described by Lobry de Bruyn (*loc. cit.*). In each experiment, 50 grams of glucose were dissolved in 700 c.c. of methyl alcohol previously saturated with ammonia, and the solutions set aside for three months. The deposition of the crystalline product commenced in about thirty days, and only material which separated spontaneously in this manner was used in our work. The condensation takes place very slowly, although, curiously enough, the similar reaction between ammonia and galactose is comparatively rapid, and, judging from the polarimetric results obtained, is complete in three days.

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* So far, this compound has not been isolated in the pure state, but the amino-group must be present in the ε-position (*Ber.*, 1911, **44**, 132; 1912, **45**, 3763). The reducing group and the α-hydroxyl group are thus unsubstituted, as indicated above.

Glucoseimine shows very slight mutarotation in water, but this seems due to the speed with which equilibrium is established. Moreover, the compound is partly decomposed when attempts are made to isolate mutarotatory forms by any process of crystallisation, and thus the material has to be used in the form in which it separates during its preparation. A specimen was, however, preserved in a sealed tube in the dark for a year, in the hope that the transformation $\beta \longrightarrow \alpha$ would proceed slowly in the solid state. The following polarimetric results were then obtained:

| Solvent. | *c.* | Specific rotation. |
|---|---|---|
| Water ............................ | 1·882 | +19·4 → 22·1 (constant for 12 hours) |
| ,, ............................ | 4·605 | 16·7 → 22·6 ( ,, ,, ,, ) |
| Aqueous methyl alcohol ...... | 1·932 | 20·4 → 21·2 ( ,, ,, 48 ,, ) |
| Aqueous pyridine ............... | 4·636 | 18·4 → 21·8 ( ,, ,, ,, ). |

Equilibrium was very quickly established in each case, and the end values recorded gradually altered owing to decomposition.

### *Action of Ammonia on Methyl-alcoholic Solutions of Sugar Derivatives.*

The following experiments were undertaken for reasons given in the introduction.

#### *Sucrose.*

Fifteen grams of dry sucrose were shaken with 200 c.c. of methyl alcohol previously saturated with ammonia. The activity ($\alpha + 9{\cdot}03^\circ$ for $l = 2$) remained constant for forty days and subsequently sucrose separated gradually during a period of eight months. The mother liquor contained the unaltered sugar, and no nitrogen compounds were detected.

#### *α-Methylglucoside.*

A solution of 50 grams of α-methylglucoside in 400 c.c. of methyl alcohol saturated with ammonia, maintained a constant rotation for five days, after which the solution deposited the glucoside in large prisms. This interrupted the polarimetric record, but, at intervals during eight months, the crystalline crops were removed, and in each case found to consist of the unaltered glucoside.

### *Tetramethyl Methylglucoside.*

The proportions used were exactly the same as those given above. The specific rotation of the solution remained quite unaffected during several weeks, and the material was recovered unaltered.

### *Gluconolactone.*

10·6 Grams of pure crystalline gluconolactone were dissolved in 120 c.c. of concentrated aqueous ammonium hydroxide (D 0·880), and the solution kept in a vacuum desiccator until all the solvent had been removed. The solid, crystalline residue was drained on porous porcelain, and purified by solution in the minimum amount of water at 60° and fractional precipitation with absolute alcohol. The first material to separate consisted almost entirely of ammonium gluconate, mixed, however, with gluconamide, which also constituted the bulk of the more soluble crops. By frequent repetition of the method of purification, a fairly complete separation of the two products was obtained, but the process was extremely tedious, and was complicated by the ready transformation of the acid amide into the ammonium salt.

*Ammonium gluconate* crystallises in flat prisms, which decompose at 154°, and show in aqueous solution $[\alpha]_D + 14{\cdot}5^\circ$ for $c=5$.

Found, $C=33{\cdot}57$; $H=7{\cdot}40$; $N=6{\cdot}76$.

$C_6H_{11}O_7{\cdot}NH_4$ requires $C=33{\cdot}80$; $H=7{\cdot}10$; $N=6{\cdot}57$ per cent.

All attempts to convert the salt into the acid amide were unsuccessful.

Gluconamide also crystallises in prisms, which decompose at 128°, with the evolution of gas. The specific rotation in aqueous solution was $[\alpha]_D + 20{\cdot}24^\circ$ ($c=5$), but this value is not permanent owing to the addition of water. The purest specimen of the compound obtained still contained a small quantity of the ammonium salt (Found, $C=36{\cdot}08$; $H=6{\cdot}82$. $C_6H_{13}O_6N$ requires $C=36{\cdot}92$; $H=6{\cdot}72$ per cent.).

It should be stated that an attempt to repeat the above reaction, using larger quantities of material, gave only the ammonium salt and no trace of the acid amide. This was doubtless due to the prolonged evaporation of the solvent.

### *Action of Ethylamine on Glucose.*

The action of a cold alcoholic solution of ethylamine on glucose results in an equilibrium being established between the constituents and the condensation product. Twenty-four grams of glucose (1 mol.) were dissolved by shaking with 1 litre of absolute ethyl alcohol containing 12 grams of ethylamine (2 mols.) The optical activity of the solution rapidly diminished, and, after nine days, a constant lævorotation was recorded. The condensation was nevertheless incomplete, and the reaction was therefore continued for four months, after which the solvent was removed in a vacuum. The residue crystallised readily, but showed a marked tendency to become gelatinous during filtration. On the basis of analysis, the polarimetric effect of hydrolysis, and titration of the ethylamine thus liberated, it was shown that the product, although apparently homogeneous, contained about 30 per cent. of unaltered glucose. The preparation, however, yielded crystalline nuclei which were of use in the isolation of the pure compound by the following method.

Glucose (1 mol.) was dissolved by shaking with anhydrous ethylamine (3 mols.). The solution rapidly set to a clear, transparent jelly. A small quantity of absolute alcohol was then added, and the mixture vigorously shaken with a nucleus obtained as described above. The jelly was thus resolved into a crystalline mass, which proved to be the desired condensation product in a state of purity. The yield was nearly quantitative. Analysis of a specimen dried at 60°/15 mm. gave:

C=46·46; H=8·34; N=6·62.

$C_8H_{17}O_5N$ requires C=46·32; H=8·21; N=6·76 per cent.

*Ethylaminoglucose* crystallises in pointed prisms, melting and decomposing at 107—108°. The compound is hydrolysed by water in the cold, and therefore reduces Fehling's solution, and reacts alkaline. The alcoholic solution, in the absence of moisture, is neutral to litmus, and is only slowly decomposed at the boiling point. The following mutarotation was detected in ethyl-alcoholic solution:

| | $[\alpha]_D$. | | $[\alpha]_D$. |
|---|---|---|---|
| $c=0·8416$ | $-21·98°$ | $\longrightarrow$ | $-12·48$ |
| $c=0·7704$ | $-28·56$ | $\longrightarrow$ | $-12·34$ |

This optical change, which was complete in one hour, was not due to partial hydrolysis promoted by the presence of moisture in the alcohol, as dilution to half the concentration with the same solvent had practically no effect on the activity, even after heating the solution to 66° for four hours in a thermostat.

This result is significant, as similar treatment with 50 per cent. alcohol resulted in complete hydrolysis, the specific rotation, calculated on the weight of glucose formed, then altering to +52·2°. The stability of the iminoglucoside, when heated with anhydrous alcohol, also affords an index of the mechanism of biose formation from glucoseimine.

*Formation of By-products in the Condensation.*—When the reaction was carried out in alcoholic solution, the solvent acquired a strong odour resembling that of pyridine. This by-product was volatile, and was obtained, along with the excess of alkylamine, in the alcohol recovered by distillation. The liquid was neutralised with $N/2$-hydrogen chloride, and the liquid again distilled at 50°/20 mm. The crystalline residue consisted of ethylamine hydrochloride, and the distillate once more contained the unknown base in the free state. Hydrochloric acid was then added until the odour of pyridine disappeared, and the solution evaporated to dryness on a water-bath. A very small crystalline residue of the ethylamine salt remained, and presumably the salt of the base had undergone dissociation and subsequent volatilisation.

### *Action of Ammonia on Fructose in Methyl-Alcoholic Solution.*

Finely powdered fructose (50 grams) was dissolved by shaking with 300 c.c. of methyl alcohol previously saturated with ammonia. The filtered solution was preserved in a well-stoppered bottle, and kept in the dark for thirty-three days. During this time the liquid gradually acquired a brown colour, crystals were deposited on the sides of the bottle, and the optical activity of the solution steadily diminished until the liquid was quite inactive.

The solid product was proved by analysis, determination of the specific rotation ($-78{\cdot}7°$ in water), and conversion into the acetyl derivative (m. p. 170°) to be the substance $C_{12}H_{20}O_8N_2$, isolated by Lobry de Bruyn in a similar reaction.

The mother liquor, which yielded the above compound, was preserved in the dark for an additional nine months, during which time it remained quite inactive. On removal of the solvent in a vacuum, a brown syrup was obtained, which solidified to a glass. This, when dissolved in a small quantity of methyl alcohol and precipitated by the addition of ether, gave a yellow, amorphous, somewhat deliquescent solid. Repeated precipitation effected the removal of the colouring matter and the deliquescent impurities, and, after drying in a vacuum at 60°, *fructoseazine* was isolated as a white powder, which decomposed, after preliminary softening, at 125°. The solubilities resembled those of fructose:

Found, $C=44{\cdot}85$; $H=5{\cdot}88$; $N=9{\cdot}10$.

$C_6H_9O_4N$ requires $C=45{\cdot}28$; $H=5{\cdot}66$; $N=8{\cdot}80$ per cent.

The compound was quite inactive in aqueous solution, even after heating for one hour at 50° with 2 per cent. hydrochloric acid. It reduced Fehling's solution on warming, and gave off ammonia when heated with sodium hydroxide. No ammonia was, however, liberated on heating with either methyl or ethyl alcohol.

The compound did not give the carbylamine test, and the absence of the amino-group was confirmed by the negative result obtained on treatment with nitrous acid. When heated with phenylhydrazine and acetic acid, phenylglucosazone was produced in excellent yield. This was identified by the melting point (204—205°) and by the specific rotation in acetic acid solution ($[\alpha]_D$ −80·3°).

The formation and constitution of this derivative of fructose is discussed in the introduction.

### *Condensation of Glucose with Diethylamine.*

Owing to its instability, the product of this reaction could not be isolated in the pure state. The anhydrous sugar (1 mol.) was added to a 33 per cent. solution of diethylamine (2 mols.) in ethyl alcohol, and the mixture shaken at intervals during a period of several weeks. The glucose passed slowly into solution, and the optical activity of the liquid gradually diminished and finally became constant. After removal of the solvent in a vacuum, a clear syrup was obtained, which analysis showed to be a mixture of the condensation product and glucose. The total product was accordingly dissolved in a large excess of ethyl alcohol containing 50 per cent. of diethylamine and kept at 20° for twenty days. During this time the activity again diminished, and again became constant. The solvent and excess of the base were removed in a vacuum. The syrupy residue was now freely soluble in anhydrous diethylamine, and a 20 per cent. solution in this solvent was accordingly preserved for ten days, after which the reagent was removed in a vacuum, and the residual syrup purified by solution in alcohol and precipitation with ether until the washings were no longer alkaline. The gelatinous product was then drained on porous porcelain, but as the use of recrystallising media rendered the mass syrupy, no further purification was possible. Owing to the instability of the compound, the analyses had to be carried out without delay, and the results for carbon and hydrogen were only approximate (Found, $N = 5{\cdot}71$; $C_{10}H_{21}O_5N$ requires $N = 5{\cdot}95$ per cent.). The compound is rapidly decomposed by water, and reduces Fehling's solution, diethylamine being liberated during the process. The specific rotation in methyl-alcoholic solution ($c = 1{\cdot}911$) was +11·5°, but this value rapidly altered, and can only be regarded as approximate.

### *Condensation of Glucose with Dimethylamine: Formation of Dimethylaminoglucose.*

Sixteen grams of glucose (1 mol.) were fixed with 700 c.c. of absolute methyl alcohol containing 8 grams of dimethylamine (2 mols.), and the mixture shaken at intervals during four months. On filtration and removal of the solvent at 30°/20 mm., a clear syrup remained, which crystallised incompletely. The total product was redissolved in alcoholic dimethylamine, and the above treatment repeated until no further alteration in rotatory power took place. The syrup ultimately obtained, in solubility and behaviour towards reagents, resembled diethylaminoglucose. Analysis of a specimen dried over phosphoric oxide gave:

$C=46{\cdot}05$; $H=8{\cdot}17$.

$C_8H_{17}O_5N$ requires $C=46{\cdot}37$; $H=8{\cdot}21$ per cent.

The use of trimethylamine, in an experiment duplicate in every other respect to that described above, gave a solution which showed no alteration in rotatory power when kept for five months. The glucose was, moreover, recovered unaltered, and no derivative containing nitrogen was detected.

Negative results were also obtained in attempts to condense glucose with diphenylamine, acetanilide, or methylanilide.

The authors are indebted to the Carnegie Trust for a research grant in aid of the investigation.

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## XXVIII.—*The Form of Extinction Curves: Cobalt Nitrate Solutions.*

By Thomas Ralph Merton, B.Sc.(Oxon.).

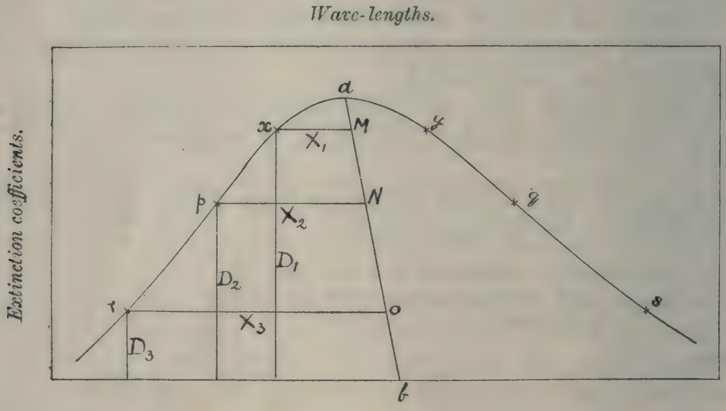
In emission spectra the distribution of intensity in spectral lines has been the subject of numerous investigations, and has in many cases been found to conform with definite laws. In the case of absorption spectra, however, no attempt appears to have been made to express the shape of extinction curves according to any law, largely, no doubt, on account of the large number of apparently anomalous shapes in which they occur. It has been shown by the author (*Proc. Roy. Soc.*, 1912, *A*, **87**, 138) that the superposition of two or more extinction curves may account for the form of apparently complicated curves. It would seem, in fact, simpler to assume that all apparently complicated curves are in reality due to the superposition of curves of simple form than to attempt to express them by any mathematical laws.

The object of the present investigation has been to find some solution which exhibits a single absorption band unaffected by the presence of other superposed bands, and to examine the form of the extinction curve.

An instance of this kind has been found to occur in the case of solutions of cobalt nitrate, which have a single absorption band in the visible spectrum.

The method of investigation and the apparatus used has been described in a previous communication (this vol., p. 124).

FIG. 1.



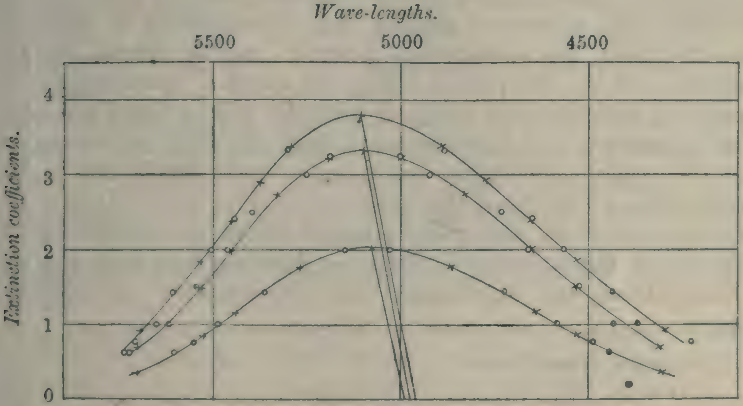
The *D*-lines of a sodium flame were superposed on each absorption spectrum, and the wave-lengths were calculated by means of a carefully drawn interpolation curve. It was found that the standard density plate used showed slightly diminished density below wave-length 4100. As a precaution, no measurements were made below 4250. Kahlbaum's nickel-free cobalt nitrate was used. It was partly dehydrated over calcium chloride in a vacuum, and the amount of cobalt in it was estimated.

It has been found that the form of the absorption curve can be expressed within the limits of experimental error in a simple mathematical form. The manner in which this has been arrived at can best be understood by reference to Fig. 1. The curve given indicates the general form of the extinction curve of a solution of cobalt nitrate. The curve is found to be symmetrical about the straight line *ab*, drawn from the maximum through the points *M*, *N*, and *O*, which are found by bisecting the distances *x y*, *p q*, and *r s* (these being any points of equal extinction on opposite sides of the absorption band).

It has been found that the form of the curve about the line *ab* may be expressed by the formula $-\log y = c^2x^2$, where $y$ is any density ($D_1$, $D_2$, and $D_3$) relative to the density at the maximum, $x$ the corresponding distance from the line *ab* ($X_1$, $X_2$, $X_3$), and $c^2$ a constant depending on the nature of the substance. This formula has been found to hold for cobalt nitrate solutions within the limits of experimental error.

In Fig. 2 are given curves of the extinctions of three aqueous solutions. The circles indicate the determined points, and the crosses the values calculated by the formula.

FIG. 2.



It will be seen that the points calculated are in good agreement with the values found. Attention must be drawn to the fact that the constant $c^2$ is not independent of the concentration, but becomes greater as the solution is diluted, that is to say, the band becomes narrower. The magnitude of this can be best appreciated by calculating the "half-widths" of the bands, that is to say, the values of $x$ when $y = 0{\cdot}5$. The concentrations, together with the values of $c^2$, the half-widths, and extinction coefficients at the maximum, were as follows:

| Concentration, grams of cobalt per litre (approximate). | $c^2$. | Extinction coefficient (at maximum). | Half-width. |
|---|---|---|---|
| 22 | 1·523 | 2·04 | 444 |
| 37 | 1·405 | 3·35 | 463 |
| 42 | 1·262 | 3·8 | 488 |

(For convenience of calculation the values of $x$ were measured in units of 1000 Å.U.)

The fact that the solution does not obey Beer's law is indicated by the fact that $c^2$ alters with the concentration, and also that the lines about which the curves are symmetrical do not meet at a common point at zero extinction. The points at which these lines cut the axis are, of course, obtained by extrapolation, and in consequence great weight must not be attached to their exact values, but attention may be drawn to the fact that the point appears to move towards the violet with increasing concentration, whilst the wave-length of the maximum moves towards the red.

Measurements of the extinction curves in alcohol solutions indicate that the formula gives as good results in the solvent as in aqueous solutions. It may be pointed out that the expression is not entirely empirical, this form of equation having been used by Michelson and others to express the distribution of light in emission lines. No explanation, however, can be offered for the inclination of the line about which the curve is symmetrical. It seems very probable that curves of this type will be found for many other substances, and it is suggested that this may be the normal form of a single absorption band, most bands being due to the superposition of curves of this type.

Some evidence at least may be looked for in the changes of the constants of the equation in different solvents, and with changes of temperature, and experiments in this direction are now in progress.

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# XXIX.—*The Influence of Water on the Partial Pressures of Hydrogen Chloride above its Alcoholic Solutions.*

By William Jacob Jones, Arthur Lapworth, and Herbert Muschamp Lingford.

Previous communications dealing with certain properties of hydrogen chloride in alcoholic solution (T., 1908, **93**, 2187; 1910, **97**, 19; 1911, **99**, 917, 1427, 2242) have dealt with the experimental evidence which shows conclusively that, when small quantities of water are added to such solutions, the chemical activity of the hydrogen chloride is greatly depressed; it was also shown that this effect cannot be distinguished in kind from that produced by the addition of a very weak anhydro-base, such as an amino-compound, to an aqueous solution of hydrogen chloride in water.

The substantial agreement between the quantitative results obtained by several entirely different experimental methods of attack offers support for the solvate theory of acids, which appears far more definite and satisfactory than the data which led Thomsen to formulate that theory (*Thermochemische Untersuchungen*, ii, 430–444; compare also *Thermochemistry*, Ramsay's Text Books of Physical Chemistry, pp. 88 and 81), or the varied considerations which have led many other chemists at various times to adopt the theory in one modification or another (compare, for example, A. Werner, *New Ideas on Inorganic Chemistry*, Hedley's Translation, 1911, p. 210 *et seq.*).

Apart altogether from the chemical interpretation of the results, the data now available establish the view that the thermodynamic potential of hydrogen chloride dissolved in absolute alcohol is depressed by the addition of water, and that to this depression may be traced:

(i) The anticatalytic effect of water in esterification (Goldschmidt), the decomposition of ethyl diazoacetate (Bredig), and other catalytic processes in which the alcohol itself takes a direct part (compare, for example, Reid, *Amer. Chem. J.*, 1909, **41**, 499 *et seq.* In this connexion, also, Acree, *ibid.*, 471; Lapworth and Partington, T., 1910, **97**, 33; Hardman and Lapworth, *ibid.*, 1911, **99**, 2246).

(ii) The anticatalytic effect of water on acid catalysis during reactions in which the alcohol plays no direct part (Lapworth, T., 1908, **93**, 2188, 2189; Dawson, *ibid.*, 1911, **99**, 1).

(iii) The hydrolytic effect of water on salts of weak bases in alcoholic solution (T., 1908, **93**, 2198; 1910, **97**, 19 *et seq.*, and 217 *et seq.*)

(iv) The reduction caused by water on the electromotive force of the hydrogen electrode in alcoholic hydrogen chloride.

Many of the foregoing methods lead to results which are more or less comparable, but only if used in solutions to which the term "dilute" might reasonably be applied, and in such instances as the influence of the non-ionised part of the acid or its non-ionised salts may clearly be either distinguished from that of the ionised acid or neglected.

Other methods of detecting changes in the thermodynamic potential of dissolved substances are those depending on measurements of vapour tensions of solvent or solute, and the intimately associated phenomena of the osmotic pressures and the cryoscopic and ebullioscopic behaviour of the solutions. Of these, the last three are difficult of application to the particular case of alcoholic hydrogen chloride for fairly obvious reasons, but these reasons do not apply so forcibly to determinations of the partial vapour tension of the hydrogen chloride.

Methods of measuring partial pressures of volatile constituents of liquid mixtures have been worked out with success by numerous investigators, including Gahl (*Zeitsch. physikal. Chem.*, 1900, **33**, 178), Abegg and Riesenfeld (*ibid.*, 1902, **40**, 84), Konowalov (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 910), Perman (T., 1901, **79**, 718; 1903, **83**, 1168), Gaus (*Zeitsch. anorg. Chem.*, 1900, **25**, 236), and McLauchlan (*Zeitsch. physikal. Chem.*, 1903, **44**, 600).

Perman and Price (*Trans. Faraday Soc.*, 1912, **8**, i, 1) have recently made a very successful and simple application of the bubbling method for measurements of the vapour pressures of concentrated aqueous solutions, and found that saturation of the air used for aspiration was attained with remarkable ease. For that case, however, the pressures to be estimated were considerable, while in the cases with which the present authors are dealing, the partial pressures are frequently relatively minute, and prolonged contact of the gas with the liquid is obviously a necessary condition. In the present series of experiments, saturators of the type devised by Gahl were employed where the time taken for any bubble of gas to pass from the bottom of the spiral to the top was at least eight seconds, and these saturators appeared to be quite efficient, as the results were independent of the speed of bubbling.

The volume of gas bubbled through the solutions was determined by passing it first of all through absolute alcohol and determining the weight of this liquid carried away. The gas subsequently entered the solution under examination, and was finally scrubbed with distilled water; the weight of hydrochloric acid carried over was subsequently determined by titration with accurately standardised barium hydroxide.

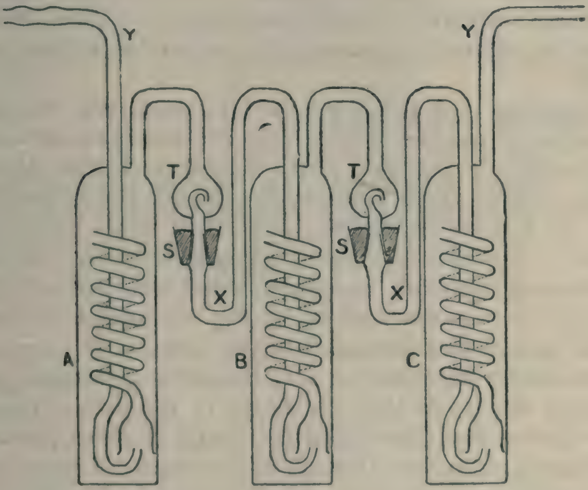
The device of passing the gas through the liquids in the order mentioned has something of novelty, and has the great recommendation that the composition of the liquid under examination, namely, that in the second vessel (the effective volume of which was about 150 c.c.), remains as nearly as possible constant even after prolonged aspiration. The principle may prove useful in other instances.

The three vessels were constructed wholly of glass and joined together in the manner indicated in the appended figure.

The saturators, which were originally much as shown, but without the bulb-traps, *T*, *T*, were united by ground glass joints, *S*, *S*, with mercury seals, and when set up the combination could be immersed completely in the water of a thermostat at 25° ± 0·05, so that only the vertical end-pieces, *Y*, *Y*, emerged.

In certain cases it was found at the end of an experiment that drops of liquid were present in the lower parts, *X*, *X*, of the bent tubes joining the vessels; as it was thought possible that this might be the result of spraying, the bulb-traps, *T*, *T*, were added. It was found that no detectable quantity of liquid was deposited in these, so that the deposition was in all cases due to a slight condensation of the vapour as the result of slight cooling in the upper portion of these tubes near the surface of the water. This phenomenon could not appreciably affect the results obtained, as all the vaporised alcohol from *A* passed into *B*, whilst the slight deposition in the entry tube of *B* was compensated for by the removal from *B* of the amount deposited, by resaturation of the gas in the main bulk of liquid in this vessel, and the whole of the hydrogen chloride carried over from *B* was carried into *C*, and there retained. The gas, after passing through *C*, was always passed through a shallow layer of water in a subsidiary wash-bottle, but invariably proved to be free from all detectable traces of hydrogen chloride. The pressure of the gas escaping from the third vessel was therefore practically identical with that of the atmosphere at the time of the experiment. The dehydrated alcohol used was prepared from commercial absolute alcohol by boiling with calcium turnings until a portion of the clear liquid set to a jelly on addition of a few drops of water (compare T., 1910, **97**, 24), when it was

FIG. 1.



distilled, the first and last portions being rejected. The alcohol obtained had $D_{4^\circ}^{25^\circ}$ 0·78493 without reduction to vacuum. Squibbs (Landolt-Börnstein, "Tabellen," p. 360) gave the value 0·78496), and Mendeléeff 0·78522 (*ibid.*, p. 359).

For the preparation of the moist alcohols used, either this material or, in one or two cases, carefully redistilled commercial absolute alcohol was used and mixed with distilled water, the percentage of water present being checked in each case by determination of the density.

The hydrogen chloride solutions were prepared by passing the carefully dried gas into the alcohol contained in a vessel which was cooled by immersion in a stream of cold water, and their precise compositions subsequently checked by titration against carefully standardised barium hydroxide solution and by density determinations.

All solutions were used very shortly after preparation, and were prepared and preserved in vessels made wholly of glass, from which they were transferred to the aspiration apparatus without exposure to the air.

Hydrogen was used as the gas for aspiration, and was generated by the action of purified zinc on dilute hydrochloric acid, and was passed successively through dilute potassium hydroxide solution, 10 per cent. silver nitrate solution, 30 per cent. potassium hydroxide solution, and pure sulphuric acid, then over dry potassium hydroxide (in sticks), and finally phosphoric oxide. Immediately before entering the first aspiration vessel the purified hydrogen was brought to the temperature of the thermostat by passing it through a glass spiral immersed in the bath.

In preliminary experiments, air, instead of hydrogen, had been used, but it was found that the values of the partial pressure for a given solution thus determined fell nearly in direct proportion to the volume of air passed through the solution; it may be added, however, that the value of the partial pressure obtained by extrapolation to the value zero for the volume of air used was, within the limits of experimental error, identical with the almost unvarying value obtained with hydrogen. Some colour always developed in the solution when air was used, and yellow drops appeared in the tubes joining the three sections of the apparatus; these signs of chemical change were entirely absent when hydrogen was employed.

### *Calculation of Partial Pressures from Experimental Results.*

If $M$ was the mean atmospheric pressure in mm. of mercury during an experiment, then $M + 20$ represented with sufficient accuracy the pressure of the mixed alcohol vapour and hydrogen leaving the vessel $A$, and $M+11$ the pressure of mixed gases leaving the vessel $B$.

The vapour pressure of ethyl alcohol at 25° is 59·50 mm. (Ramsay and Young, *Phil. Trans.*, 1886, **177**, 155), so that, if the gases and liquid are in equilibrium in the space at the top of $A$,

$$\frac{59\cdot5}{M+20}=\frac{\text{Vol. of alcohol vapour}}{\text{Vol. of } H_2 + \text{vol. of alcohol vapour}}.$$

If $W$ was the weight of alcohol evaporated from $A$, and its vapour density is normal at 25° and 59·5 mm., then the volume which the alcohol vapour would occupy if undiluted was:

$$\frac{W\times22410\times298\times760}{46\cdot05\times273\times(M+20)}\text{ c.c.}$$

It follows that the total volume of hydrogen and alcohol vapour was:

$$\frac{W\times22410\times298\times760}{59\cdot5\times46\cdot05\times273}\text{ c.c.,}$$

the partial pressure of the hydrogen chloride in the solution being given by

$$P=\text{total pressure in } B\times\frac{\text{Vol. of gaseous HCl removed}}{\text{Total volume of gas passing out of } B}.$$

When $q$ was the titre of hydrogen chloride removed from the second vessel in terms of $N/10$-alkali, then the volume of hydrogen chloride which had escaped from the second vessel was:

$$\frac{q\times22410\times298\times760}{10^4\times273\times(M+11)}.$$

Introducing this in the previous expression and simplifying, the following relation is obtained:

$$P=\frac{274q\times(M+11)}{10^3W\times(M+20)+274q}.$$

The question of the influence of change in the concentration of the hydrogen chloride during the course of an experiment has carefully been considered, but the decrease in quantity of the hydrogen chloride in the most extreme case, namely, experiment No. 5 on the list given later, did not amount to more than 0·5 per cent. of the whole, and the change in the amount of water present must have been even smaller; the alteration in the quantity of alcohol in the middle vessel due to its slightly lower partial pressure is partly compensated for by the increasing volume of gas due to expansion under decreasing pressure, and was also almost inappreciable in comparison with other experimental disturbances. The view that these factors are almost negligible is confirmed by comparison of the partial pressures as determined from experiments of varying duration, such as No. 4 contrasted with 5, 9 with 10, or 19 with 21. No correction for such disturbances has therefore been applied.

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | X. | XI. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0·78493 | 0·86405 | 3·188 | 0·000 | 3·135 | 54·66 | 759 | 1·3 | 4·69 | *4·69* |
| 2 | 0·78493 | 0·86405 | 3·188 | 0·000 | 3·443 | 59·94 | 759 | 1·3 | 4·69 | |
| 3 | 0·78882 | 0·86599 | 3·181 | 0·529 | 2·458 | 39·54 | 753 | 1·8 | 4·35 | *4·29* |
| 4 | 0·79306 | 0·86988 | 3·191 | 1·132 | 1·954 | 28·00 | 754 | 0·9 | 3·86 | *3·90* |
| 5 | 0·79306 | 0·86988 | 3·191 | 1·132 | 4·357 | 61·58 | 753 | 1·1 | 3·81 | |
| 6 | 0·79841 | 0·87357 | 3·188 | 1·891 | 1·636 | 18·85 | 768 | 0·6 | 3·11 | *3·13* |
| 7 | 0·80207 | 0·87643 | 3·195 | 2·452 | 4·996 | 46·34 | 759 | 1·8 | 2·50 | *2·58* |
| 8 | 0·80207 | 0·87643 | 3·195 | 2·452 | 5·748 | 54·63 | 759 | 2·8 | 2·56 | |
| 9 | as in 1 | — | 2·390 | 0·000 | 1·386 | 13·62 | 756 | 0·5 | 2·65 | *2·62* |
| 10 | ,, | — | 2·390 | 0·000 | 2·811 | 27·09 | 756 | 0·9 | 2·60 | |
| 11 | as in 3 | 0·84952 | 2·395 | 0·537 | 3·705 | 30·85 | 760 | 1·3 | 2·25 | *2·25* |
| 12 | as in 4 | 0·85257 | 2·392 | 1·150 | 1·307 | 8·39 | 750 | 1·0 | 1·74 | *1·76* |
| 13 | ,, | 0·85257 | 2·392 | 1·150 | 2·849 | 18·23 | 750 | 1·2 | 1·73 | |
| 14 | as in 6 | 0·85422 | 2·392 | 1·920 | 5·892 | 25·93 | 765 | 2·4 | 1·19 | *1·14* |
| 15 | as in 1 | 0·81716 | 1·168 | 0·000 | 4·663 | 13·88 | 751 | 1·0 | 0·806 | *0·81* |
| 16 | ,, | 0·81716 | 1·168 | 0·000 | 4·960 | 14·94 | 751 | 0·8 | 0·815 | |
| 17 | 0·78701 | 0·81968 | 1·171 | 0·285 | 7·245 | 16·98 | 744 | 2·5 | 0·634 | *0·66* |
| 18 | 0·78701 | 0·81968 | 1·171 | 0·285 | 10·310 | 24·14 | 745 | 1·6 | 0·633 | |
| 19 | as in 3 | 0·82009 | 1·165 | 0·548 | 3·198 | 6·01 | 762 | 0·9 | 0·506 | *0·52* |
| 20 | ,, | 0·82009 | 1·165 | 0·548 | 5·903 | 11·11 | 762 | 0·9 | 0·509 | |
| 21 | ,, | 0·82009 | 1·165 | 0·548 | 8·401 | 15·71 | 763 | 0·8 | 0·506 | |
| 22 | as in 4 | 0·82304 | 1·170 | 1·173 | 4·964 | 4·41 | 757 | 1·9 | 0·241 | *0·27* |
| 23 | as in 1 | — | 0·751 | 0·000 | 4·106 | 6·35 | 760 | 1·5 | 0·419 | *0·42* |
| 24 | ,, | — | 0·751 | 0·000 | 5·061 | 7·74 | 760 | 1·6 | 0·414 | |
| 25 | 0·78900 | 0·80979 | 0·752 | 0·579 | 4·809 | 2·81 | 759 | 1·8 | 0·158 | *0·22* |
| 26 | 0·78900 | 0·80979 | 0·752 | 0·579 | 5·251 | 3·07 | 759 | 1·8 | 0·158 | |
| 27 | as in 1 | 0·79049 | 0·275 | 0·000 | 3·202 | 1·23 | 764 | 0·6 | 0·104 | *0·11* |
| 28 | ,, | 0·79049 | 0·275 | 0·000 | 6·232 | 2·55 | 764 | 0·7 | 0·111 | |
| 29 | as in 17 | 0·79439 | 0·274 | 0·288 | 5·058 | 0·67 | 761 | 1·6 | 0·036 | *0·06* |
| 30 | ,, | 0·79439 | 0·274 | 0·288 | 5·849 | 0·79 | 760 | 1·4 | 0·037 | |

The experimental data, with the deduced partial pressures of hydrogen chloride, are summarised in the preceding table, where are given:

Under column I, the reference number of the experiments.

Under column II, the values of $D_{4^\circ}^{25^\circ}$ (without correction to vacuum) for the samples of anhydrous or moist alcohols from which the solutions of hydrogen chloride were prepared.

Under column III, the values of $D_{4^\circ}^{25^\circ}$ for the hydrogen chloride solutions.

Under column IV, the numbers of gram-molecules of hydrogen chloride per litre initially present in the solution in *B*.

Under column V, the numbers of gram-molecules of water per litre present in the solution in *B*.

Under column VI, the values of *W*, or weight of alcohol (corrected to vacuum) evaporated from the vessel *A*.

Under column VII, the values of *q*, or the titres of hydrogen chloride removed from the second vessel in c.c. of *N*/10-alkali.

Under column VIII, the values of $M$, the mean atmospheric pressure in mm., if necessary, prevailing during the aspiration.

Under column IX, the mean rates of bubbling in litres of gas per hour.

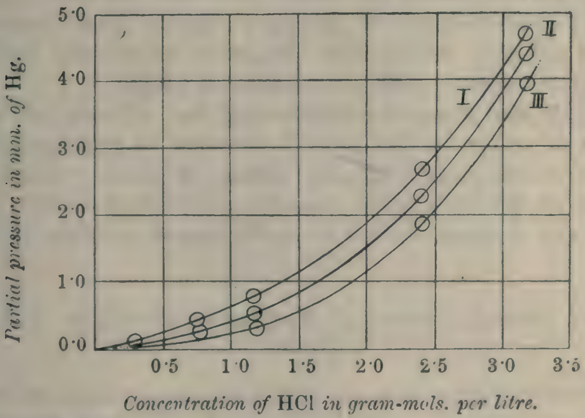
Under column X, the deduced partial pressures of hydrogen chloride in mm. of mercury.

Under column XI, the values of $P$ calculated by means of the formula given on p. 262.

The discrepancies between parallel experiments indicate agreement within 0·06 mm., or about 2·5 per cent., for pressures of 2·50 mm. or more; for lower pressures the margin of discrepancy in the absolute values is still smaller, although the percentage error becomes greater; the lowest pressures agree with one another within less than 0·01 mm.

There is, however, good reason to distrust the very lowest values found in moist alcohol, namely, those obtained in experiments 25 or 26, and 29 or 30. These, although concordant amongst themselves, appear anomalous when contrasted with the others by any method, graphic* or formal; the numbers in column XI are probably much nearer the true values than those found experimentally. Careful repetition of the experiments 25 and 26 gave results practically identical with those in column X, and as the very lowest value in the case of absolute alcoholic solution (experiments 27 and 28) appears quite normal, it appears most likely that for some reason the experimental method, when applied to solutions with such small concentrations of hydrogen chloride in

FIG. 2.



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* This is best seen by plotting the logarithms of the partial pressures against logarithms of the concentration of hydrogen chloride.

moist alcohol, gives abnormally low results. On the other hand, it is possible, though improbable, that the depression caused by very small quantities of water increases much more rapidly at these low concentrations of hydrogen chloride than the other results would suggest.

In Fig. 2 are given curves indicating the manner in which the partial pressure of the hydrogen chloride varies with the concentration of this gas in alcohol containing a fixed quantity of water.

Curve I refers to anhydrous solutions.

Curve II refers to solutions containing 0·5 gram-mol. $H_2O$ per litre.

Curve III refers to solutions containing 1·0 gram-mol. $H_2O$ per litre.

It may be noted, on comparing the different quantities of water which correspond with the same partial pressures, that, at 4 to 5 mm., 1 gram-molecule of water has the apparent effect of removing $\frac{1}{4}$ gram-molecule of hydrogen chloride from the sphere of action; at 1·5 mm. or less, the proportion apparently removed is about $\frac{1}{2}$ gram-molecule over a considerable range.

In Fig. 3 are given curves showing the influence of varying quantities of water on the partial pressures of hydrogen chloride when the concentration of the latter is fixed. The relative depression caused by a given quantity of water is seen to increase markedly as the concentration of the hydrogen chloride diminishes.

### *Values of Partial Pressure of Hydrogen Chloride in Anhydrous Alcohol.*

In endeavouring to find an expression adequately to represent the relation between partial pressures and concentrations of hydrogen chloride and alcohol vapour, use was made of Duhem's differential equation:

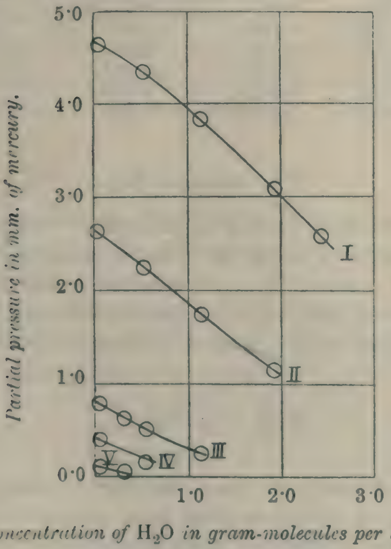
$$\frac{d\,.\log p}{dx} + x\frac{d\,.\log P}{dx} = 0,$$

where $P$ here represents the partial pressure of the hydrogen chloride, $p$ that of the alcohol, and $x$ the number of gram-molecules of hydrogen chloride per gram-molecule of alcohol in the liquid phase.

Dolezalek applied this formula to the case of aqueous hydrogen chloride on the assumption that $\log p$ was a linear function of $x$. Integration led to the equation $\log P = a\log x + k$, where $a$ and $k$ are constants, and the calculated values over a range from $P = 0·52$ to 277 were fairly consistent with the experimental values only within a margin of about 15 per cent. (*Ber. Deut. physikal. Ges.*, 1903, **5**, 4). In the case of alcoholic hydrogen chloride, a similar degree of concordance is noticed, but when consideration is paid to the fact that saturated hydrogen chloride in alcohol is between 10 and 11*N* by volume, it becomes clear that the algebraic expression equated to $\frac{d\,.\log p}{dx}$ must contain a power of $x$ not less than the second.

FIG. 3.

Curve I. $HCl = 3{\cdot}19$ *gram-molecules per litre*
,, II. $HCl = 2{\cdot}39$ ,, ,, ,,
,, III. $HCl = 1{\cdot}17$ ,, ,, ,,
,, IV. $HCl = 0{\cdot}75$ ,, ,, ,,
,, V. $HCl = 0{\cdot}275$ ,, ,, ,,



Putting
$$\frac{d\,.\log p}{dx} = a' + b'x + d'x^2,$$

and placing this in Duhem's equation, we obtain an equation of the type:

$$\log P = a_0 \log x + b_0 x + d_0 x^2 + k_0,$$

where four constants are present. The employment of the term in $x^2$ would be unnecessary if it were desired to include only the values for anhydrous solutions in the table on p. 258, where its influence is only that of a very small correction term, but its introduction should permit of more accurate extrapolation beyond those limits to both higher and lower values.

In calculating the values of $x$, the densities at 25° of anhydrous alcohol containing various strengths of hydrogen chloride, as above given, were used; the density of 10·45 volume-normal hydrogen chloride at 25° was found to be 0·96651.

The formula becomes:

$$\log_{10} 10P = 1{\cdot}284 \log X + 0{\cdot}01106X + 0{\cdot}000115X^2 - 0{\cdot}256,$$

where $X = 100x$.

The following table shows the applicability of this formula:

| $n$*. | $x$. | $P$ (observed). | $P$ ("calc.") |
|---|---|---|---|
| (10·45 | 0·82 | 760·0 (nearly) | 760·0 |
| 3·188 | 0·1965 | 4·69 | 4·63 |
| 2·39 | 0·1451 | 2·63 | 2·63 |
| 1·168 | 0·0696 | 0·811 | 0·808 |
| 0·751 | 0·0444 | 0·417 | 0·423 |
| 0·275 | 0·0162 | 0·108 | 0·107 |

### *The General Form.*

Largely no doubt in virtue of the four "constants," equations of similar type apply when $n$, the volume-normality of the hydrogen chloride, is used instead of $x$, its relative molecular concentration. Not only is this the case with the anhydrous solution, but also with solutions containing water; that is, a general equation of the type:

$$\log_{10} \pi = a \log_{10} C + bC + dC^2 + k$$

applies to all solutions when $\pi = 100P$

$$C = 10n.$$

Moreover, the values of the "constants" vary quite regularly with the amount of water, so that each constant may be expressed in terms of $w$, the number of gram-molecules of water present per litre of solution; thus:

$$a = 1{\cdot}3171 + 1{\cdot}0306w + 0{\cdot}3907w^2.$$
$$10^3 b = 3{\cdot}847 - 12{\cdot}11w - 3{\cdot}851w^2.$$
$$10^4 d = 1{\cdot}2633 + 0{\cdot}398w + 0{\cdot}10798w^2.$$
$$k = 0{\cdot}4392 - 1{\cdot}2481w - 0{\cdot}5014w^2.$$

These numbers, it may be noted, are intended for use in the neighbourhood of the region covered by the measurement in the table on p. 258. Their application for the calculation at somewhat higher pressures is partly justified by their agreement with the fact that the concentration of alcoholic hydrogen chloride saturated at 25° and atmospheric pressure, is between 10 and 11 normal, by volume, even in presence of small quantities of water. The values for the partial pressures, calculated by means of the above formulæ, are given, within 0·01 mm., in column XI of the table on p. 258; the order of agreement is within the limits of experimental error, with the exception possibly of the doubtful cases mentioned on p. 259.

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* $n$ is used to represent the concentration of the hydrogen chloride in gram-molecules per litre.

The fact that the method described in the present paper gives satisfactory results only over a range where the concentrations of hydrogen chloride are considerable, prevents any direct comparison of these with previous observations on the influence of water on the properties of alcoholic hydrogen chloride. It is hoped that by an extension of the earlier experiments to higher concentrations of acid such a comparison may prove of considerable theoretical interest, but further discusssion may be reserved until more data have been accumulated; the case of electromotive forces of concentration cells containing alcoholic hydrogen chloride will be dealt with specially.

## *Summary.*

(1) The partial pressures of hydrogen chloride in the saturated vapours of alcoholic solutions of this gas have been measured at 25° over a considerable range.

(2) The partial pressures increase very rapidly with the concentration, although much less rapidly than with aqueous solutions.

(3) The partial pressures are reduced very considerably by the presence of small quantities of water, the relative fall increasing as the concentration of hydrogen chloride diminishes.

(4) The formula of Dolezalek applies, in its simplest form, over a very small range only; in an extended form it applies over a wide range, whilst a similar but complicated formula may be used to calculate the influence of change of concentration of either hydrogen chloride or water or both.

The authors beg to acknowledge their indebtedness to the Government Grant Committee of the Royal Society for a grant, from which much of the cost of the investigation was defrayed.

Chemical Laboratories,
The University, Manchester.

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# XXX.—*The Presence of Helium in the Gas from the Interior of an X-Ray Bulb.*

By Sir William Ramsay, K.C.B.

Last July a brief statement was made in a letter to *Nature* to the effect that the residual gas extractable by heating the glass of an *X*-ray bulb contained a measurable trace of helium, in which the neon spectrum could also be identified. The object of this note is to describe the experiment in greater detail, and also to state that the result has been confirmed.

In the first experiment the glass of four very deeply coloured *X*-ray bulbs, furnished me by the kindness of my friend, Sir James Mackenzie Davidson, was placed in a combustion tube of hard glass; junction was made with a Töpler's pump by thick-walled indiarubber tubing, protected from possibility of leakage by a mercury guard-tube. Pure oxygen was admitted to the tube four times, and removed by pumping until a vacuum tube in circuit showed green phosphorescence; in this way all adhering air was removed from the surface of the glass. The temperature of the tube was then raised to redness, and the gases extracted by pumping. This gas was collected in a small tube containing mercury; in order to expel any air from the walls of the tube, the mercury was boiled until no more bubbles of gas escaped; it was then inverted over the end of the capillary tube of the pump. The gas which it contained was sucked into a bulb through an inverted syphon, closed by a ground-on cap, which could be removed below the mercury of the trough; in this way a stopcock is avoided, and leakage is rendered quite impossible. Connected with the bulb was a small bulb containing about 0·2 gram of cocoanut charcoal; the charcoal-bulb had been heated to the temperature of boiling sulphur, and all gas removed by pumping again until green phosphorescence was seen in the attached vacuum-tube. The gas from the glass was then left in contact with the charcoal cooled with liquid air for about half-an-hour, in order that the oxygen might be completely absorbed. The residual gas in the bulb was next made to enter a capillary tube of very narrow bore, furnished with an electrode sealed in at its upper end. This was done by allowing mercury to enter the bulb from below, in the same manner as mercury enters the barrel of a Töpler pump. The mercury in the capillary tube was then frozen with liquid air; there is thus a double advantage: the gas is confined, and the mercury vapour is condensed, so that its spectrum no longer appears in the capillary tube. The frozen mercury serves, moreover, as one electrode, the other being the platinum wire sealed through the end of the capillary tube.

The volume of the residual gas was not measured on this occasion, but its spectrum showed all the lines of helium with great brilliance, and at the same time some of the more brilliant of the neon red lines were faintly visible.

The second experiment was carried out differently. The exit tube of an *X*-ray bulb was connected by means of thick-walled rubber tubing with a Töpler pump, a vacuum-tube being as before in circuit. The drawn-out end of the exit tube had previously been scratched with a glass-knife, so that it could be broken through the rubber by the help of pliers. Before this was done, all air was pumped out of the connecting tube, and after the end was broken a guard-tube was slipped over the junction, and filled with mercury; leakage was thus rendered impossible. The *X*-ray bulb stood in an air-bath of asbestos card, and was heated to about 350°. The phosphorescence of the tell-tale vacuum tube was not altered when connexion was made with the *X*-ray bulb, but after heating, the spectrum showed oxygen and nitrogen and a trace of carbon dioxide to be present. About a cubic centimetre of pure oxygen was admitted into the *X*-ray bulb, so as to "wash" it out; the gases collected by means of the pump were treated as already described. The result was the same; the spectrum was that of helium, and only two of the stronger red lines of neon were visible.

The process was repeated with a second and a third *X*-ray bulb; the result was the same. The volume of the combined gases was measured; it was about 0·39 cubic millimetre.

The bulbs were then broken up, and the powdered glass was placed in a combustion tube connected with the pump with the same precautions against leak as have already been described; the combustion tube was pumped empty, and four times washed out with oxygen; and the gas given off on heating was collected. After treatment with cooled charcoal, not a trace of any gas could be seen when the mercury was run up into the capillary tube; all the gas was absorbable in cooled charcoal. This negative experiment gives strong reason for the conclusion that the inactive gas in the former experiments was not derived from any air which might have leaked in. Indeed, supposing that the 0·39 cubic millimetre of inactive gas had been derived from air, the amount of air required to furnish the helium and neon found, supposing them to have been present in the proportions in which they exist in air, would have been no less than 22 cubic centimetres.

The fact, therefore, has to be accounted for that it is possible to extract from the interior of an *X*-ray bulb helium mixed with a trace of neon in measurable quantity. Its source is, of course, a matter for conjecture; it may be that under the influence of the cathode discharge helium and neon are able to penetrate the walls of the bulb, which exclude oxygen and nitrogen. Or it is possible to imagine another explanation less likely to be received without challenge: that these gases are in some way the product of the cathode rays.

LONDON.

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## XXXI.—*Vaubel's Supposed Phenyldi-imine.*

### By MARTIN ONSLOW FORSTER and JOHN CHARLES WITHERS.

WHILE investigating the reduction of diazoaminobenzene with zinc dust in alkali, Vaubel (*Ber.*, 1900, **33**, 1711) obtained a liquid boiling at 162—164°, appearing to have the composition $C_6H_6N_2$, and regarded by him as phenyldi-imine, $C_6H_5\cdot N\colon NH$.

Our attention was attracted to this substance by two factors, namely, the improbability of its surviving the method of preparation, and the importance of studying such a type supposing it to be capable of existence. We accordingly attempted to prepare phenyldi-imine by Vaubel's process, which consists in slowly distilling the alcohol from a solution of diazoaminobenzene in alcoholic alkali to which zinc dust has been added, and then passing a current of steam through the residual liquid after acidification.

It is not clear from the meagre details furnished by Vaubel whether acidification was practised on the alkaline liquid alone or on the solid matter suspended in it; we therefore separated the solid in the earlier experiments, but finding that the liquid alone did not give oil when acidified and distilled in steam, we conclude that Vaubel allowed the solid to remain suspended in the alkaline liquid to which dilute sulphuric acid was then added. On following this course, we also obtained a yellow oil which, after being shaken with alkali to remove phenol, was divisible by distillation under 13 mm. pressure into two fractions, boiling at 67—70° and 74—75° respectively, the latter being pure aniline. The more volatile, pale yellow fraction, which should have been phenyldi-imine, was analysed several times because the empirical formula indicated, namely, $C_{18}H_{17}N_7$, was difficult to reconcile with any probable individual.

Qualitative examination of the substance, however, revealed the properties of both aniline and phenylazoimide, and we believe, therefore, that the liquid obtained in the manner described is a constant boiling mixture of those two compounds in the proportion $2C_6H_5{\cdot}N_3 + C_6H_5{\cdot}NH_2$. This conclusion is confirmed by the fact that on distilling a mixture of phenylazoimide with excess of aniline under the above-mentioned pressure, the lower fraction was a liquid agreeing in every detail, qualitative and quantitative, with the supposed phenyldi-imine which we obtained from diazoaminobenzene.

The fact that Vaubel's product has the composition $C_6H_6N_2$ is explained by the circumstance that, having been distilled under atmospheric pressure, its composition would be different from that of a product fractionated under 13 mm., and it is significant that an equimolecular mixture, $C_6H_5{\cdot}N_3 + C_6H_5{\cdot}NH_2$, would have the same percentage composition as phenyldi-imine.

Certain points in Vaubel's description of phenyldi-imine are in agreement with our hypothesis that his material is a mixture of phenylazoimide and aniline. According to his statement, it does not form salts with dilute alkalis, it is dissolved only in part by hydrochloric acid, and with sulphuric acid yields "eine eigenthümliche, weissliche, klebrige Verbindung, die sich aber bald wieder in Oel und Säure scheidet," and which doubtless consists of aniline sulphate impregnated with phenylazoimide. Furthermore, the boiling point of phenyldi-imine under atmospheric pressure was stated to be 162—164°, and the only recorded boiling point of phenylazoimide at such a high pressure is 161—162°/754 mm. Moreover, the distillation of phenyldi-imine was accompanied by extensive decomposition and the production of a white solid, the composition of which was not determined; it is highly significant that when phenylazoimide is allowed to mix with aniline at 150°, a colourless, solid base, $C_{12}H_{12}N_2$, is produced, accompanied by liberation of nitrogen (Wolff, *Annalen*, 1912, **394**, 59).

It remains to explain how this mixture is produced in the circumstances of Vaubel's experiment. Recalling the fact, already mentioned, that the solid was not removed from the alkaline liquid before acidification, it will be recognised that the supposed phenyldi-imine arose from the action of dilute sulphuric acid on a mixture of zinc dust and diazoaminobenzene. Supposing the acid to resolve the latter into aniline and diazonium salt, a portion of which becomes reduced to phenylhydrazine, this base, in action with diazonium salt, would yield a further quantity of aniline accompanied by phenylazoimide. It might be supposed that on distillation in steam, phenylazoimide would pass over alone, but we find that a faintly acid solution of aniline sulphate will yield a considerable proportion of the base when a current of steam is passed continuously through the liquid. The variety of the changes involved in this explanation will readily account for the low yield recorded by Vaubel and confirmed by our own experiments.

## EXPERIMENTAL.

Twenty-five grams of diazoaminobenzene, freshly prepared, were dissolved in 100 c.c. of alcohol, and heated with 50 c.c. of 20 per cent. aqueous sodium hydroxide and 20 grams of zinc dust during two hours, in the course of which time there distilled over 125 c.c. of liquid containing aniline and phenylhydrazine. The pale yellow oil remaining in the flask became solid on cooling, and consisted of pure diazoaminobenzene, as stated by Vaubel; this was filtered, and the alkaline filtrate, after extraction with ether, did not give an oil when acidified and distilled in steam. In subsequent experiments, therefore, the zinc and diazoaminobenzene were not removed before sulphuric acid was added, and in these circumstances a pale yellow oil slowly distilled in the steam.

The product accumulated from 225 grams of diazoaminobenzene was dissolved in ether and extracted with sodium hydroxide, from which phenol alone was recovered; on evaporating the ether after drying with sodium sulphate about 15 grams of oil remained, divided by fractional distillation under 13 mm. pressure into 4 grams boiling at 67—70° and 10 grams boiling at 74—75°, the latter consisting of pure aniline. The more volatile portion, which had a distinct odour of phenylazoimide, was redistilled, boiling at 64—65°/13 mm.:

0·1385 gave 0·3300 $CO_2$ and 0·0623 $H_2O$. C = 64·98; H = 5·03.

0·1162 „ 29·0 c.c. $N_2$ at 15° and 756 mm. N = 29·08.

$2C_6H_5{\cdot}N_3 + C_6H_5{\cdot}NH_2$ requires C = 65·22; H = 5·17; N = 29·61 per cent.

When shaken with dilute hydrochloric acid a portion dissolved, and the solution, when freed from oil by ether, gave with hypochlorite the colour characteristic of aniline, which was also indicated by diazotisation and coupling; the ethereal extract deposited phenylazoimide on evaporation, this effervescing strongly with concentrated sulphuric acid or a solution of stannous chloride in hydrochloric acid. The original substance also gave the intense colour with hypochlorite, and when reduced with stannous chloride gave aniline and nitrogen, unaccompanied by phenylhydrazine, which should be formed if phenyldi-imine were present. With concentrated sulphuric acid vigorous liberation of gas took place:

0·3003 gave with 75 per cent. $H_2SO_4$ 43·4 c.c. $N_2$ at 20·5° and 764 mm. N = 16·50.

$2C_6H_5{\cdot}N_3 + C_6H_5{\cdot}NH_2$ requires 2/3 azidic N = 16·92 per cent.

For comparison with this material an artificial mixture of phenylazoimide with considerable excess of aniline was distilled under 13 mm. pressure, yielding an early fraction boiling at 62—65°; this was redistilled and analysed, the percentages of nitrogen and two-thirds the azidic nitrogen being in close agreement with the above, from which it did not differ by any qualitative test.

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# XXXII.—*αδ-Derivatives of Adipic and β-Methyladipic Acids, and the Preparation of Muconic and β-Methylmuconic Acids.*

By HENRY STEPHEN and CHARLES WEIZMANN.

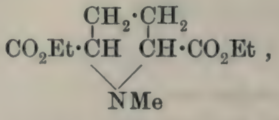
THE experiments on **αδ**-derivatives of adipic and β-methyladipic acids, of which a short account has appeared (P., 1912, **28**, 95), have been continued, and have led finally to some interesting results. The work of Markovnikov (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 381), and also the process discovered by the Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 221849), have made adipic and β-methyladipic acids accessible. It was desirable to prepare from these acids, on the one hand, **αδ**-diaminoadipic and **αδ**-diamino-β-methyladipic acids, and on the other, muconic and β-methylmuconic acids.

Considerable quantities of adipic and β-methyladipic acids have been prepared by oxidising *cyclo*hexanone and 4-methyl*cyclo*hexanone respectively with nitric acid (D 1·4), and the acids thus obtained have been brominated.

The bromination of these acids was carried out by the usual Hell-Volhard method, with the difference that thionyl chloride was used for the preparation of the acid chlorides. The use of this reagent leads to the formation of very pure acid chlorides. The product from the bromination was treated with anhydrous formic acid or alcohol according as the free acid or ester was required; and in this way we have prepared the **αδ**-dibromo-acids and esters. These dibromo-esters have also been described by Le Sueur (T., 1909, **95**, 273).

The displacement of the two bromine atoms in the above **αδ**-dibromo-compounds by the amino-group was found to be a matter of considerable experimental difficulty. The action of ammonia, both aqueous and alcoholic, leads to the formation of pyrrolidinedicarboxylic esters or acids. It was therefore thought that the treatment of the dibromo-esters with potassium phthalimide, and the subsequent hydrolysis of the diphthalimino-compounds might lead to a satisfactory result. This proved to be correct especially in the case of the **αδ**-dibromoadipic esters; but the **αδ**-dibromo-**β**-methyladipic esters were found to react with potassium phthalimide with great difficulty, and only small quantities of the diphthalimino-compounds could be obtained.

The preparation of muconic and **β**-methylmuconic acids by removing two molecules of hydrogen bromide from the corresponding dibromo-esters was also one of considerable difficulty. In this connexion, Willstätter and Lessing (*Ber.*, 1902, **35**, 2065) found that when ethyl **αδ**-dibromoadipate was treated with methylamine in benzene solution, ethyl 1-methylpyrrolidine-2:5-dicarboxylate was produced.



Le Sueur (*loc. cit.*) has also observed a similar reaction in an attempt to obtain the unsaturated ester from the same dibromo-ester, by treating the latter with mono- or di-ethylaniline, obtaining, however, the corresponding *N*-pyrrolidine compounds, analogous to that obtained by Willstätter and Lessing (*loc. cit.*). In our experiments we have studied the action of trimethylamine in alcoholic solution (33 per cent.), and triethylamine in dry benzene, on methyl and ethyl **αδ**-dibromoadipates and **αδ**-dibromo-**β**-methyladipate respectively, and have succeeded in isolating the corresponding unsaturated esters which on hydrolysis led to the acids. The yields obtained by these methods are small, due to the same tendency of ring formation, and here again the results obtained are more satisfactory in the case of the dibromo-adipic esters than with the homologue. As a further attempt to obtain the unsaturated compounds, we have treated the dibromo-esters with quinoline, but only very small quantities of unsaturated esters could be isolated.

The diacetoxy-compounds of ethyl **αδ**-dibromoadipate and ethyl **αδ**-dibromo-**β**-methyladipate have also been prepared by heating the above esters with fused potassium acetate in glacial acetic acid.

## EXPERIMENTAL.

### *Bromination of Adipic Acid.*

In order to brominate the adipic acid obtained as stated above, 100 grams of the acid were treated with 190 grams of thionyl chloride, an excess of 20 per cent. being used. The mixture was warmed on the steam-bath until the whole had assumed the liquid state, and there was no further evolution of hydrogen chloride, which requires about one hour for completion. Pure bromine (240 grams) was then added gradually during a period of forty-eight hours, and the whole continuously heated on the steam-bath until evolution of hydrogen bromide had ceased.

### *Methyl αδ-dibromoadipate,* $CO_2Me{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2Me$.

This ester was obtained by carefully adding methyl alcohol to the bromo-acid chloride prepared above, until the somewhat violent reaction had subsided. On cooling, the bromo-ester was poured into water, extracted several times with ether, the ethereal extract washed with a dilute solution of sodium hydrogen sulphite, and finally several times with water; on removal of the ether a semi-solid mass remained, which was distilled under diminished pressure. The ester (yield, 175 grams from 100 grams of adipic acid) obtained boils at 182°/10 mm., and is a colourless liquid, which on cooling partly solidifies to a white, crystalline solid.

This, after being separated from the liquid portion by pouring the mixture on a porous plate, was crystallised from ethyl alcohol, and obtained in white needles, which melted at 75°. The ester is soluble in methyl or ethyl alcohols, ether, benzene, or chloroform.

### *Ethyl αδ-dibromoadipate,* $CO_2Et{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2Et$.

This was obtained in an analogous way to the methyl ester. It also exhibited the same semi-solid state, and the solid modification of the ester was crystallised from ethyl alcohol and obtained in white needles melting at 65°. The ester distils at 195°/10 mm.; the solubility was the same as for the methyl ester, and the yield was 180 grams from 100 grams of adipic acid.

### *αδ-Dibromo-β-methyladipic Acid,*
### $CO_2H{\cdot}CHBr{\cdot}CHMe{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H$.

β-Methyladipic acid (160 grams: 1 mol.) was brominated as described above. The bromo-acid chloride was converted into the free acid by the addition of anhydrous formic acid until the reaction had ceased. A viscid, yellow oil was obtained, from which after several weeks crystals of αδ-dibromo-β-methyladipic acid separated. When recrystallised from anhydrous formic acid it is obtained in large, white, rhombic prisms, which melt at 138°. The acid is soluble in the usual organic solvents, and sparingly so in hot water:

0·2148 gave 0·2101 $CO_2$ and 0·0599 $H_2O$. C=26·6; H=3·1.
0·1665 „ 0·1941 AgBr. Br=49·9.
$C_7H_{10}O_4Br_2$ requires C=26·4; H=3·1; Br=50·3 per cent.

### *Methyl αδ-Dibromo-β-methyladipate,*
### $CO_2Me{\cdot}CHBr{\cdot}CH_2{\cdot}CHMe{\cdot}CHBr{\cdot}CO_2Me$.

This was obtained from the bromo-acid chloride on treatment with methyl alcohol. It is a colourless liquid boiling at 167—168°/12 mm., and could not be prepared in the solid form; a yield of 64 per cent. of the acid used was obtained.

### *Ethyl αδ-Dibromo-β-methyladipate,*
### $CO_2Et{\cdot}CHBr{\cdot}CH_2{\cdot}CHMe{\cdot}CHBr{\cdot}CO_2Et$.

This was prepared in an analogous manner to the above; it is a colourless liquid, which distils at 180°/10 mm., and also does not solidify; a yield of 72 per cent. of the acid used was obtained. Even when these esters were prepared by esterification of the solid αδ-dibromo-β-methyladipic acid they could not be obtained in the solid state.

### *Ethyl αδ-Diacetoxyadipate,*
### $CO_2Et{\cdot}CH(OAc){\cdot}CH_2{\cdot}CH_2{\cdot}CH(OAc){\cdot}CO_2Et$.

This ester was obtained by heating in an oil-bath 36 grams of ethyl αδ-dibromoadipate with twice the theoretical quantity of fused potassium acetate (40 grams) in a large excess of glacial acetic acid, at 160° for eight hours. The product was poured into water, the ester extracted several times with ether, and the ethereal solution shaken several times with dilute sodium carbonate solution to remove traces of acetic acid, washed with distilled water, and dried. On removal of the ether the ester was distilled, and a colourless liquid boiling at 195°/10 mm. was obtained; this, on cooling, gave a white solid, which crystallised from ethyl alcohol in small, white needles, melting at 73°. (Yield, 15 grams.) The pure diacetate can be distilled without decomposition under the ordinary pressure:

0·1466 gave 0·2861 $CO_2$ and 0·0898 $H_2O$. C=53·2; H=6·5.
$C_{14}H_{22}O_8$ requires C=52·7; H=6·8 per cent.

### *Ethyl αδ-Diacetoxy-β-methyladipate,*

$CO_2Et\cdot CH(OAc)\cdot CHMe\cdot CH_2\cdot CH(OAc)\cdot CO_2Et.$

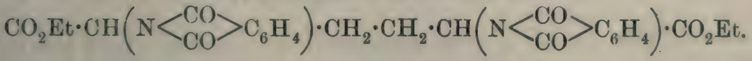
This was obtained in the same way as the previous compound. It is a white solid, which crystallises from ethyl alcohol in white needles melting at 66°, and boiling at 182°/10 mm.:

0·1022 gave 0·2031 $CO_2$ and 0·0647 $H_2O$. C=54·3; H=7·04.

$C_{15}H_{24}O_8$ requires C=54·2; H=7·2 per cent.

Both diacetoxy-compounds, like the corresponding dibromo-compounds, occur in two modifications, namely, as liquids and solids.

### *Ethyl αδ-Diphthaliminoadipate,*



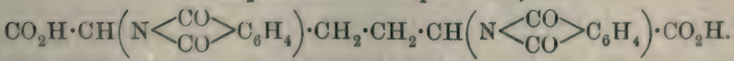
$CO_2Et\cdot CH\left(N{<}\substack{CO\\CO}{>}C_6H_4\right)\cdot CH_2\cdot CH_2\cdot CH\left(N{<}\substack{CO\\CO}{>}C_6H_4\right)\cdot CO_2Et.$

This ester was obtained by heating 50 grams of ethyl αδ-dibromoadipate with 70 grams of potassium phthalimide, using a quarter of a molecule excess of the latter, in xylene in an oil-bath at 135—140° for twenty-four hours, the xylene being gradually distilled from the product during the last hour of the heating. The crude product obtained, which was a deep honey-yellow, semi-solid cake, was then poured into water and distilled in a current of steam to remove remaining traces of xylene. On cooling, the product was extracted with carbon disulphide, which separates the excess of phthalimide from the condensation product, only the latter being soluble in carbon disulphide. The extract was then dried, the carbon disulphide removed by distillation, and the oily residue submitted to distillation under diminished pressure. A pale yellow liquid boiling at 200—210°/10 mm. was obtained, and it solidified on cooling to a white solid, which crystallised from ethyl alcohol in colourless needles melting at 115°. It is soluble in methyl or ethyl alcohols, and very soluble in carbon disulphide:

0·1731 gave 0·3976 $CO_2$ and 0·0739 $H_2O$. C=62·77; H=4·77.
0·1701 „ 7·4 c.c. $N_2$ at 18° and 754 mm. N=5·58.

$C_{26}H_{24}O_8N_2$ requires C=63·3; H=4·8; N=5·7 per cent.

### *αδ-Diphthaliminoadipic Acid,*



$CO_2H\cdot CH\left(N{<}\substack{CO\\CO}{>}C_6H_4\right)\cdot CH_2\cdot CH_2\cdot CH\left(N{<}\substack{CO\\CO}{>}C_6H_4\right)\cdot CO_2H.$

This acid was obtained from the above ester by (*a*) hydrolysis of the ester with an excess of a glacial acetic acid solution of hydrogen bromide at the ordinary temperature, or (*b*) by hydrolysis of the ester with the necessary quantity of alcoholic potassium hydroxide. In the first case (*a*), the acid was obtained directly as a solid on addition of water to the glacial acetic acid solution. In the other case (*b*), the free acid was obtained from the alkaline solution on addition of hydrochloric acid in the cold. It is a pale yellow, crystalline powder, which does not melt at 270°, and is soluble in glacial acetic acid, from which it can be crystallised. It is insoluble in water, but sparingly soluble in ethyl alcohol:

0·2016 gave 0·4434 $CO_2$ and 0·0724 $H_2O$. C = 60·00; H = 3·96.
$C_{22}H_{16}O_8N_2$ requires C = 60·5; H = 3·7 per cent.

*αδ-Diphthalaminoadipic Acid,*

$$\begin{array}{l} CO_2H\cdot CH(NH\cdot CO\cdot C_6H_4\cdot CO_2H)\cdot CH_2 \\ CO_2H\cdot CH(NH\cdot CO\cdot C_6H_4\cdot CO_2H)\cdot CH_2 \end{array}.$$

Twenty-four grams of ethyl αδ-diphthaliminoadipate were treated with a solution of 20 grams of potassium hydroxide dissolved in its own weight of water; a vigorous reaction set in, and when this had subsided the mixture was heated on the steam-bath for some time until a clear solution had been obtained. The solution was then cooled on ice and carefully neutralised with the exact quantity of 5*N*-hydrochloric acid. A solid separated, which was washed free from potassium chloride with water, and crystallised from hot water. It was obtained as a fine, crystalline powder, which when dried at the ordinary temperature contains two molecules of water of crystallisation:

0·1960 gave 0·3804 $CO_2$ and 0·0736 $H_2O$. C = 52·3; H = 4·7.
0·7510 lost 0·0532 at 100°. $H_2O$ = 7·08.
$C_{22}H_{20}O_{10}N_2,2H_2O$ requires C = 52·00; H = 4·7; $H_2O$ = 7·08 per cent.

A sample of the acid dried at 100° gave the following results:

0·1252 gave 0·2570 $CO_2$ and 0·0516 $H_2O$. C = 55·3; H = 4·3.
$C_{22}H_{20}O_{10}N_2$ requires C = 55·9; H = 4·2 per cent.

The acid after being dried at 100° is insoluble in hot water, but soluble in sodium carbonate solution, from which it is again precipitated in the insoluble form on addition of hydrochloric acid. On fusion the acid begins to decompose at 119° with evolution of carbon dioxide.

*αδ-Diaminoadipic acid,*

$$CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

was obtained by treating the above acid with concentrated hydrochloric acid, the free acid being obtained by neutralising the solution of the hydrochloride with dilute aqueous ammonia.

The crude acid was converted into the copper salt by boiling with an aqueous suspension of copper hydroxide, filtering, and allowing the copper salt to crystallise. It is obtained in this way in blue, crystalline plates:

0·5840 gave Cu = 22·7.

0·4527 lost 0·0591 at 110°. $H_2O = 13·02$.

$C_6H_{10}O_4N_2Cu,2H_2O$ requires Cu = 23·2; $H_2O = 13·05$ per cent.

The dried copper salt is insoluble in water. These observations are in agreement with those of Sörensen and Andersen (*Zeitsch. physiol. Chem.*, 1908, **56**, 266).

### *The Action of Trimethylamine and Triethylamine on Methyl and Ethyl αδ-Dibromoadipates, and Methyl and Ethyl αδ-Dibromo-β-methyladipates respectively.*

Methyl *αδ*-dibromoadipate (64 grams) was heated in sealed tubes with a slight excess over the theoretical quantity of a 33 per cent. alcoholic solution of trimethylamine for thirty-eight hours at 100—105°. The product was diluted with anhydrous ether in order to separate trimethylamine hydrobromide, filtered, and the filtrate poured into water, extracted with a further quantity of ether, and the ethereal extract washed several times with dilute hydrochloric acid. The dried ethereal extract was evaporated, and the residue submitted to distillation under diminished pressure.

A colourless liquid began to distil at 185°/12 mm., and solidified on cooling to a white, crystalline solid, which was unsaturated and free from bromine; after crystallisation from ethyl alcohol it melted at 158°, which is the melting point of methyl muconate (*Ber.*, 1902, **35**, 1148). The yield was about 3 grams of solid ester, which was hydrolysed by means of methyl-alcoholic potassium hydroxide to the free acid. This was crystallised from hot water, and a white, crystalline powder melting and decomposing at 298° was obtained.

Replacing the methyl ester by the ethyl ester made no difference in the actual yield of muconic acid. The ethyl ester of muconic acid distilled at 200°/12 mm.

In a similar way ethyl and methyl *αδ*-dibromoadipates were heated with triethylamine diluted with dry benzene in a sealed tube for the same time at 110°. The same unsaturated esters were obtained, but the yield did not improve.

The washings obtained by treating the ethereal extract with hydrochloric acid were evaporated nearly to dryness with animal charcoal, filtered, and then evaporated to dryness under diminished pressure; a white, crystalline solid was obtained, which on treatment with moist silver oxide gave the characteristic odour of trimethylamine. After removing the silver chloride formed, the filtrate was concentrated in a vacuum, and a viscid, syrupy liquid remained, which, however, did not distil, and nothing of definite composition could be isolated.

*Ethyl β-methylmuconate*, $CO_2Et{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CO_2Et$, was obtained in a similar way to that stated above when ethyl αδ-dibromo-β-methyladipate was treated with trimethylamine in 33 per cent. alcoholic solution, or with triethylamine in dry benzene. As in the previous case, the yields were very poor, and the substitution of the methyl ester caused no alteration in the result. A basic substance was apparently removed, as in the case of the adipic compound, on washing the ethereal extract with hydrochloric acid; but on similar treatment no compound of definite composition could be isolated. The ethyl ester is a colourless liquid boiling at 175°/10 mm., which showed a tendency to crystallise, but remained in a semi-solid condition.

*Methyl β-methylmuconate*, $CO_2Me{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CO_2Me$, obtained by the same method as in the case of the ethyl ester described above, is a colourless liquid boiling at 145°/9 mm. It could not be obtained in the solid state.

In some experiments we have found that ethyl-alcoholic barium hydroxide also gave very good results when used to hydrolyse these unsaturated esters, especially in the case of the esters of β-methylmuconic acid. The two esters above were hydrolysed with alcoholic barium hydroxide, and the free β-methylmuconic acid was obtained by precipitating the barium salt with dilute hydrochloric acid.

*β-Methylmuconic acid*, $CO_2H{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CO_2H$, is a white solid which crystallises from hot water as a crystalline powder; it may also be crystallised from acetic acid, and melts and decomposes at 235°:

0·1054 gave 0·2077 $CO_2$ and 0·0486 $H_2O$. C=53·74; H=5·12.

$C_7H_8O_4$ requires C=53·84; H=5·12 per cent.

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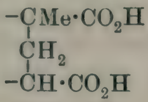
# XXXIII.—*The Chemistry of the Glutaconic Acids. Part VII. The Normal and Labile Forms of αγ-Dimethylglutaconic Acid and their Reduction to* cis-*αγ-Dimethylglutaric Acid.*

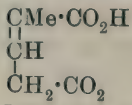
By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

THE experiments described in the preceding parts of this series have led to the conclusion (T., 1912, **101**, 1740) that the so-called stereoisomeric forms of the "mobile" acids of this group are in reality structural isomerides, which may be represented in the case of, for example, α-methylglutaconic acid, by the expressions:



$$\begin{array}{l}-\mathrm{CMe{\cdot}CO_2H}\\ \mathrm{CH_2}\\ -\mathrm{CH{\cdot}CO_2H}\end{array}$$

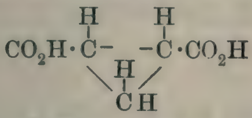
Normal state.



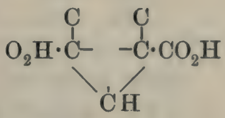
$$\begin{array}{l}\mathrm{CMe{\cdot}CO_2H}\\ \mathrm{CH}\\ \mathrm{CH_2{\cdot}CO_2}\end{array}$$

Labile state.

The conclusion was also drawn (*ibid.*, p. 871) that there is considerable analogy between the normal states of these acids and the corresponding 1:3-dicarboxylic acids of the aromatic series, and that the normal state of, for example, glutaconic acid, may be considered as analogous to *iso*phthalic acid:

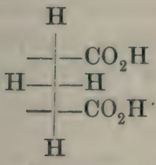


Glutaconic acid.

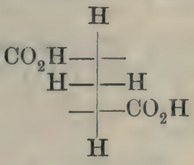


*iso*Phthalic acid.

and that, therefore, this state is to be regarded as the meso- or non-resolvable form, and as having a *cis*-structure in which both carboxyl groups are on the same sides of the terminal tetrahedrons; the racemic or *trans*-modification being incapable of existence *:

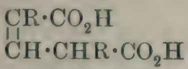


Meso-form.



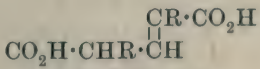
Racemic form.

At the same time the weight of experimental evidence points to the conclusion that the labile forms of the acids of this series also possess a structure in which both carboxyl groups are on the same sides of the terminal tetrahedrons, and that it is only in special circumstances, that is to say, when groups of high molecular weight enter the molecule, that sufficient stability is conferred on this state to render the *trans*-modification capable of isolation (*ibid.*, p. 1739):



$$\begin{array}{l}\mathrm{CR{\cdot}CO_2H}\\ \mathrm{CH{\cdot}CHR{\cdot}CO_2H}\end{array}$$

*cis*-Labile acid.



$$\begin{array}{r}\mathrm{CR{\cdot}CO_2H}\\ \mathrm{CO_2H{\cdot}CHR{\cdot}CH}\end{array}$$

*trans*-Labile acid.

There appears to be only one way by which the *cis*-configuration of the two states of these acids can be definitely proved, and that is by choosing some derivative of glutaconic acid substituted by the same alkyl group on both the α- and γ-carbon atoms, and by reducing both the normal and labile states of this acid to the corresponding derivative of glutaric acid. If our assumption is correct, then both the normal and labile forms should yield the *cis*-modification of the substituted glutaric acid, thus:

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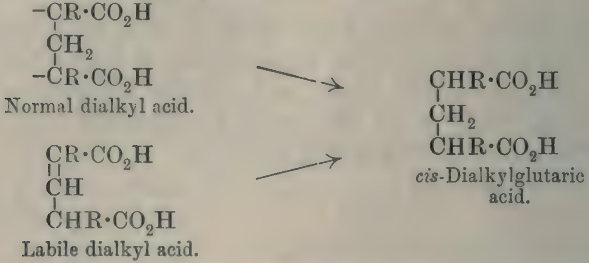
* This conclusion is also supported by the experiments carried out by Mr. C. R. Young, of this University, which show that the brucine salt of glutaconic acid cannot be separated into fractions differing in their rotatory power.



$$\begin{array}{l}-CR\cdot CO_2H\\ \quad|\\ \;\;CH_2\\ \quad|\\ -CR\cdot CO_2H\end{array} \longrightarrow \begin{array}{l}CHR\cdot CO_2H\\ |\\ CH_2\\ |\\ CHR\cdot CO_2H\end{array} \longleftarrow \begin{array}{l}CR\cdot CO_2H\\ \|\\ CH\\ |\\ CHR\cdot CO_2H\end{array}$$

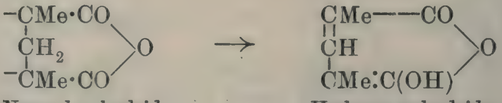
Normal dialkyl acid.

*cis*-Dialkylglutaric acid.

Labile dialkyl acid.

The acid best suited for our purpose was evidently αγ-dimethylglutaconic acid, because the well-defined forms of αγ-dimethylglutaric acid, melting at 128° and 141° respectively, are readily recognisable; and, moreover, the presence of any *trans*-modification mixed with its *cis*-isomeride could be detected owing to the production of the equilibrium mixture of the two forms which melts at 105°.

αγ-Dimethylglutaconic acid has been described in Part II. of this series (T., 1911, **99**, 2217), and was shown to yield both the normal and hydroxy-anhydride, the former being converted into the latter on distillation:



$$\begin{array}{l}-CMe\cdot CO\\ \quad|\\ \;\;CH_2\\ \quad|\\ -CMe\cdot CO\end{array}\!\!>\!O \longrightarrow \begin{array}{l}CMe\text{---}CO\\ \|\\ CH\\ |\\ CMe\!:\!C(OH)\end{array}\!\!>\!O$$

Normal anhydride.

Hydroxy-anhydride.

Both the normal and hydroxy-anhydride yielded the normal acid melting at 147° on treatment with water, and it was not found possible to isolate the labile modification of the acid. Since that time, however, more experience has been gained respecting the treatment necessary for the isolation of the labile acids of this series, and we now find that under suitable conditions the hydroxy-anhydride of αγ-dimethylglutaconic acid can be converted into the labile form of the acid which is a well-defined substance melting at 118°. Labile αγ-dimethylglutaconic acid, like the other labile acids of this series, is readily converted into the normal acid on treatment with mineral acids, but is remarkably stable towards alkali, and can be boiled with a concentrated aqueous solution of this reagent without undergoing change. It was therefore reduced by sodium amalgam, in aqueous solution, without carbonic acid.

The completely reduced product was found to be *cis*-$\alpha\gamma$-dimethylglutaric acid melting at 128°; no trace of the *trans*-modification or of the equilibrium mixture could be detected.

The reduction of the normal form of $\alpha\gamma$-dimethylglutaconic acid was effected under similar conditions, but in the first instance it was proved by experiment that this form of the acid is not affected by concentrated alkali. It will be remembered that the normal form of $\beta$-methylglutaconic acid is completely converted into the salt of the labile acid on being boiled with a concentrated aqueous solution of potassium hydroxide, and it therefore follows that, if the normal form of $\alpha\gamma$-dimethylglutaconic acid behaved in the same manner, reduction in alkaline solution might cause a partial conversion of one form into the other, and hence detract from the value of the experiment. As a matter of fact, it was found that the normal acid is quite unaltered even on prolonged boiling with concentrated aqueous alkali, and the reduction was therefore carried out under the same conditions as were employed with the labile acid; at the same time, a similar experiment was conducted in the presence of excess of carbonic acid, and in both cases the completely reduced product was found to be *cis*-$\alpha\gamma$-dimethylglutaric acid melting at 128°.

During these experiments it was noticed that the normal form of the acid resists the action of the reducing agent to a greater degree than the labile modification, for whereas the latter is completely reduced after the second treatment with excess of sodium amalgam, the former requires to be treated at least four times before a product is obtained which no longer decolorises permanganate.

## EXPERIMENTAL.

### *Labile $\alpha\gamma$-Dimethylglutaconic Acid*, $CO_2H\cdot CMe\colon CH\cdot CHMe\cdot CO_2H$.

After several unsuccessful attempts to prepare this substance it was ultimately obtained by treating the hydroxy-anhydride with a concentrated aqueous solution of alkali hydroxide under the following conditions. Five grams of the hydroxy-anhydride were mixed with 20 c.c. of a 50 per cent. solution of potassium hydroxide, and kept with constant shaking at a temperature of 30°. At the end of five hours the clear, colourless solution was diluted with water and mixed with rather less than the theoretical amount of hydrochloric acid required to neutralise the free alkali in the solution. The liquid was transferred to a separating funnel, covered by ether, and then treated with slightly more than the amount of hydrochloric acid required to combine with the remaining quantity of sodium salt in solution. The acid was added in small portions at a time, and after each addition the funnel was vigorously shaken. The ether was then separated, dried, and evaporated, when it left an oily residue which solidified on being scratched, and was obtained in microscopic needles melting at 118° by crystallisation from a little water:

0·2072 gave 0·4023 $CO_2$ and 0·1143 $H_2O$. C=52·95; H=6·13.
$C_7H_{10}O_4$ requires C=53·2; H=6·3 per cent.

The mother liquor from the ether extraction yielded on further extraction an acid which evidently contained a small amount of the normal acid.

The labile acid is more soluble in water and in ether than its normal isomeride, but does not differ from it in its behaviour towards metallic salts. There is a marked difference in the behaviour of the two compounds towards acetyl chloride, for when the labile acid is treated with this reagent under the same experimental conditions that produce the normal anhydride from the normal acid (T., 1911, **99**, 2235), it is converted into the hydroxy-anhydride melting at 75°.

### *The Reduction of the Labile Acid to* cis-*αγ-Dimethylglutaric Acid.*

The reduction was effected by sodium amalgam in aqueous solution. Ten grams of the acid dissolved in dilute alkali were treated with successive portions of 29 grams of sodium as 3 per cent. amalgam, the solution being cooled throughout the reduction by running water. Since the acid extracted from the acidified product by ether still possessed the property of decolorising alkaline permanganate, the reduction was repeated with the same amount of amalgam as before. The final product, which was solid, did not reduce permanganate; it was crystallised from water, and obtained in needles melting at 128°. (Found, C=52·41; H=7·53. $C_7H_{12}O_4$ requires C=52·5; H=7·5 per cent.)

The acid was characterised as *cis*-αγ-dimethylglutaric acid by conversion into the anhydride melting at 95° by the action of acetyl chloride. Excepting for a trace of a solid of lower melting point, this acid appeared to be the only substance formed by the reduction of the labile acid.

### *The Reduction of the Normal Acid to* cis-*αγ-Dimethylglutaric Acid.*

In the first instance it was proved by experiment that the normal acid is not affected by prolonged boiling with 20 per cent. aqueous alkali, and for this purpose the acid dissolved in the alkali was heated to the boiling point for five hours. The acid was extracted practically unchanged, from the acidified solution, by ether. The reduction was then carried out in precisely the same manner as with the labile acid, only in this case the product did not cease to decolorise permanganate until the reduction had been effected four times. The recrystallised acid melted at 128° (Found, C=52·38; H=7·58. $C_7H_{12}O_4$ requires C=52·5; H=7·5 per cent.), and gave the characteristic anhydride of *cis*-αγ-dimethylglutaric acid on treatment with acetyl chloride. In this case also no trace of the *trans*-acid could be detected, although, as was to be expected from the repeated extractions with ether, the yield of the saturated acid was considerably less than in the case of the labile acid.

In order to show that the alkali hydroxide generated during the reduction had no effect on the nature of the product, a similar reduction was carried out in the presence of excess of carbonic acid. The same result was obtained.

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## XXXIV.—*The Measurement of Tryptic Protein Hydrolysis by Determination of the Tyrosine Liberated.*

By SAMUEL JAMES MANSON AULD and THOMAS DUNCAN MOSSCROP, B.Sc.

OF the numerous methods described for following the course of protein hydrolysis, that described by Brown and Millar (T., 1906, **89**, 145) apparently offers many advantages, since it is volumetric in character, easy of manipulation, and in the hands of these authors gave good results. The method, in brief, is based on the estimation, by absorption of bromine, of the tyrosine formed during tryptic digestion, and is carried out along the lines suggested by J. H. Millar (*Trans. Guinness Research Laboratory*, 1903, Part I.). The tyrosine-containing liquid is acidified with hydrochloric acid to which sodium bromide is added, and the solution thus obtained is titrated with standard sodium bromate solution. The product of reaction is dibromotyrosine.

We had occasion to study this method during the preliminary work attending another investigation, and found that, as originally described, the method is difficultly workable, but can be made useful by the introduction of several modifications.

### *Use of Starch and Potassium Iodide as Indicator.*

J. H. Millar originally used the persistence of the yellow colour of bromine to mark the end-point of the reaction, but also states that starch and potassium iodide may be used as indicator of free bromine. The latter method was adopted by Brown and Millar.

In colourless solutions the yellow colour induced by excess of bromine may certainly be used to show the completion of the reaction, but this is impossible in ordinary protein digests, and the use of starch and iodine is also impossible, as a little consideration might show, since hydrochloric acid itself will liberate sufficient iodine from potassium iodide to cause coloration of the starch. We tried the effect of acidifying the solution with other weaker acids (such as phosphoric, citric, and acetic acids), but on keeping for a period equivalent to the length of time occupied by a titration they also liberate iodine and mask the end-point.

### *Use of Methyl-violet as Indicator.*

Attempts were made to utilise the oxidising power of bromine in discharging the colour of organic dyestuffs, but with only partial success. Good results were, however, obtained by using the well-known stain, Gentian-violet, which shows marked colour changes. Gentian-violet is the commercial name given to a mixture of Methyl-violet, Crystal-violet, and dextrin, and the colour changes were found to be due to the Methyl-violet (pentamethylpararosaniline hydrochloride). In the acid solution used for titration this dyestuff becomes olive-green, and the addition of sodium bromate or traces of free bromine causes a sharp change to a deep bluish-violet. The change is very marked and exceedingly sharp, although the colour fades after several minutes. Excess of bromine or sodium bromate solution discharges the blue colour, changing it to a dirty yellow.

### *Rate of Bromination of Tyrosine.*

Tyrosine rapidly takes up bromine to form dibromotyrosine, and the absorption at first is very rapid, but falls off considerably, under the conditions of titration, towards the end of the reaction, as is shown by the following case.

Twenty-five c.c. of $N/25$-tyrosine solution in 5 per cent. hydrochloric acid and 20 c.c. of 20 per cent. sodium bromide solution were titrated with $N/20$-sodium bromate; 0·5 c.c. of the latter was added at a time as long as the bromine was absorbed at once, and then two drops at a time until the reaction was complete.

| | *N*/20-Sodium bromate used. C.c. | Tyrosine brominated. Per cent. | Time taken for absorption of bromine. |
|---|---|---|---|
| Up to | 7·0 | 55·1 | 3·0 sec. (normal shaking) |
| | 8·0 | 62·9 | 3·5 ,, |
| | 9·0 | 70·8 | 6·0 ,, |
| | 11·0 | 86·6 | 9·0 ,, |
| | 12·0 | 94·5 | 25·0 ,, |
| | 12·4 | 97·6 | 2 min. |
| | 12·6 | 99·2 | permanent after 30 min. |

The falling off of the rate of bromination shows the impossibility, in any case, of the use of starch and potassium iodide as indicator, and precludes the use of any indicator within the experimental liquid, since free bromine may be present for a short time in the solution, and yet be absorbed by the tyrosine on keeping.

## *Method Used.*

*Indicator.*—Methyl-violet or Gentian-violet may, however, be satisfactorily used as an outside indicator. The colouring matter is made of 1 per cent. strength in 70 per cent. alcohol, and about ten drops of the solution are added to 10 c.c. of 5 per cent. hydrochloric acid. This liquid is dotted over a white tile in the usual manner, and tested with the experimental liquid from time to time. With a little practice and after doing a preliminary titration the end of the reaction, as indicated by the formation of the blue colour, may be detected with accuracy.

On the tile, water alone produces a very similar colour, but dilute acid effects no change. Free bromine water of all strengths will not give the colour change, but does so with practically the same delicacy when dissolved in sodium bromide solution. This may be due to the formation of an unstable perbromide or similar compound with the Methyl-violet, or possibly to its action as nascent bromine (as in the actual titration of acid bromide solution with sodium bromate), the sodium bromide solution acting as $NaBr,xBr$.

*Procedure.*—The solution to be titrated is made of not more than 5 per cent. acidity with hydrochloric acid. A lower concentration of acid than 2 per cent. turns the indicator blue, whilst a higher concentration than 5 per cent. turns it yellow. To the acid solution is added 15—20 c.c. of 20 per cent. sodium bromide, and the liquid is then titrated with *N*/20-sodium bromate. Brown and Millar used *N*/5-sodium bromate solution for titration, but since it is seldom that more than 1 c.c. of solution of such strength is required, more accurate results are obtained by using the more dilute liquid.

Towards the end of the reaction at least thirty seconds should elapse between successive additions of the sodium bromate, and the reaction is best carried out in a stoppered bottle, which can be vigorously shaken after each addition.

Under these conditions sufficiently accurate, comparable results can be obtained to make the method extremely useful. Dibromotyrosine only is apparently formed. Sodium bromate corresponding with 6 molecules of bromine were added to a known weight of tyrosine dissolved in dilute hydrochloric acid, and mixed with sodium bromide, and the mixture allowed to remain for twenty-four hours. At the end of that time the excess of bromine was estimated, and the amount absorbed was found to be practically only 2 molecules.

The following results were obtained with tyrosine and tyrosine-containing mixtures of strengths unknown at the time:

| Weight of tyrosine used. Gram. | *N*/20-Bromate solution used. C.c. | Weight of tyrosine found. Gram. | Error. Per cent. |
|---|---|---|---|
| 0·1274 | 9·80 | 0·1274 | nil. |
| 0·1460 | 11·45 | 0·1495 | +2·3 |
| 0·1559 | 11·80 | 0·1576 | 1·09 |
| *0·1000 | 7·60 | 0·1010 | 1·0 |
| *0·0481 | 3·65 | 0·0483 | 0·4 |

* In solutions containing tyrosine, leucine, asparagine, and ammonium chloride.

Experiments carried out with edestin digested in dilute sodium carbonate solution with trypsin, and corrected for the bromine absorbed by the protein, confirmed Brown and Millar's contention that the method can be used for determining tyrosine in presence of proteins and other early cleavage products, and also that practically the whole of the tyrosine is liberated in the first stages of tryptic digestion.

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## XXXV.—*The Solubility of Sulphanilic Acid and its Hydrates.*

By James Charles Philip.

In the course of another research it became desirable to ascertain exactly the conditions of stability of the different hydrates of sulphanilic acid. According to earlier investigations (see Laar, *J. pr. Chem.*, 1879, **20**, 242; *Ber.*, 1881, **14**, 933), both dihydrate and monohydrate exist, but the conditions of temperature and concentration under which they separate from solution have not been determined. The solubility of sulphanilic acid has accordingly been measured at a number of temperatures between 0° and 55°, whilst, in addition, the composition of the solid phase in equilibrium with the saturated solution was determined in each case.

The investigation has shown that the stable solid in contact with the saturated solutions is dihydrate from 0° to 21°, monohydrate from 21° to 40°, and anhydrous acid from 40° upwards. In previous determinations of the solubility of sulphanilic acid (see Dolinski, *Ber.*, 1905, **38**, 1835), this change in the character of the solid phase as the temperature rises has been overlooked, and the attempt has been made to represent the variation of solubility with temperature as a continuous curve. As will be seen from the determinations of solubility recorded below, this cannot be done. In some cases, indeed, two distinct values were obtained for the solubility at a given temperature, and investigation revealed the fact that the difference in solubility was associated with a difference in the solid phase present.

The equilibrium between the solid hydrates and the water vapour in the surrounding atmosphere also presents points of interest. Chief among these is the difference in the behaviour of the dihydrate and the monohydrate in regard to dehydration. Under conditions in which the monohydrate is unaltered, the dihydrate loses all its water, and leaves the anhydrous acid. This is probably due to suspended transformation in the case of the monohydrate, but it has been frequently observed that the rate of dehydration of the dihydrate exhibits no change at the point corresponding with the monohydrate. This fact suggests that the molecules of the dihydrate, when deprived of water, may yield those of the anhydrous acid directly, without passing through the monohydrate stage, and further evidence of this kind, if obtainable, would throw light on the manner in which the water molecules are attached in compounds containing water of crystallisation.

Whilst this appears to be the normal course of dehydration of the dihydrate, it was observed in a few cases that the process stopped at the monohydrate stage, although the conditions were those in which other samples of the dihydrate had lost all their water.

From experiments in which the hydrates were kept in closed vessels over sulphuric acid of different strengths, and weighed from time to time, the dissociation pressures were deduced. At 20° the dihydrate remains of constant weight in an atmosphere with an aqueous vapour pressure higher than about 16·5 mm. of mercury, whilst the corresponding limit for the monohydrate is about 12 mm. of mercury. The latter figure was confirmed by direct measurement of the dissociation pressure in a tensimeter.

## EXPERIMENTAL.

The sulphanilic acid employed in the investigation was obtained by recrystallisation of the best commercial acid. The purity of the recrystallised material was established by dissolving a known quantity in water, and titrating with a carefully standardised sodium hydroxide solution.

In the determination of solubility the point of equilibrium was reached from both sides. In one tube, water was stirred up with excess of sulphanilic acid; in another tube, a solution which had been saturated at a somewhat higher temperature was treated similarly. The two tubes were immersed in a constant temperature bath, and the stirring was continued for six to seven hours at least. The equality of the values obtained for the solubility in the parallel experiments was a guarantee that equilibrium between solid and solution had really been reached. In some cases, where intermittent shaking was employed instead of continuous stirring, the time of contact of solid with solution was correspondingly longer.

When sufficient time had been allowed for the attainment of equilibrium, two samples of the saturated solution were drawn into separate pipettes through cotton-wool plugs, and immediately discharged into weighed flasks. In this way, known weights of saturated solution were obtained, and the sulphanilic acid present was then estimated by titration with standard sodium hydroxide solution.

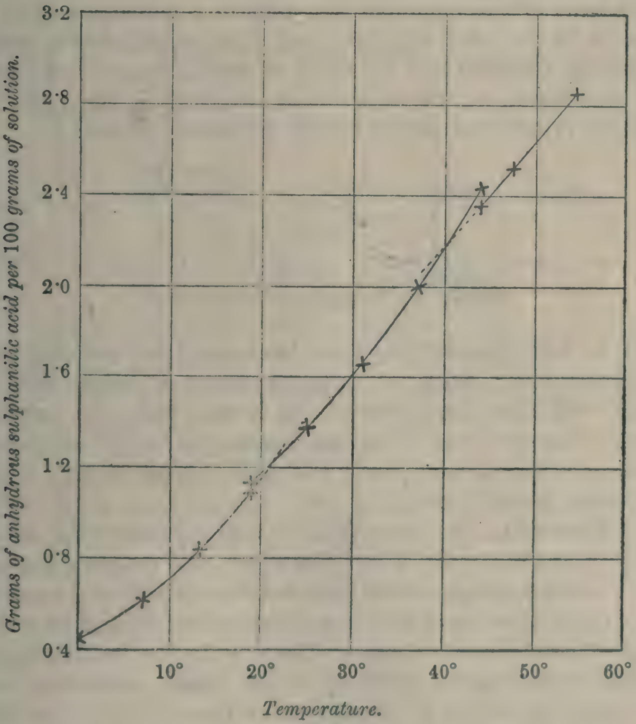
When the extracts had been made, the remaining solution, along with the excess of solid, was thrown on a filter, and the liquid was removed as completely as possible with the aid of a pump. After the solid had been further dried by pressing between filter paper for about ten minutes, a portion was weighed out and left overnight in a vacuum desiccator containing concentrated sulphuric acid. In these circumstances the water of crystallisation of sulphanilic acid is rapidly and completely removed. The dihydrate contains 17·2 per cent. of water, and the monohydrate 9·42 per cent., so that this method of examination showed clearly whether the solid in equilibrium with the saturated solution had been dihydrate, monohydrate, or anhydrous acid.

The results obtained for the solubility are recorded in the following table, and are represented graphically in Fig. 1. The temperatures shown in the table are corrected values, based on a comparison of the thermometers actually used with a standard instrument.

| Temp. | Grams of anhydrous acid per 100 grams of solution. | Solid phase. |
|---|---|---|
| 0·0° | 0·444 | dihydrate |
| 7·2 | 0·622 | ,, |
| 13·3 | 0·841 | ,, |
| 18·9 | 1·093 | ,, |
| 18·9 | 1·137 | monohydrate |
| 25·1 | 1·384 | ,, |
| 31·1 | 1·662 | monohydrate |
| 37·2 | 2·004 | ,, |
| 44·0 | 2·44 | ,, |
| 44·0 | 2·36 | anhydrous acid |
| 47·5 | 2·52 | ,, |
| 54·5 | 2·85 | ,, |

Particular interest attaches to the figures obtained at 18·9° and 44·0°. In two experiments at the former temperature, different

FIG. 1.



values of the solubility were recorded, and examination of the solid phase in each case showed that the higher value was obtained in presence of the monohydrate, which is metastable at 18·9°, whilst the lower solubility was given by the stable dihydrate. Similarly, at 44·0°, the higher value of the solubility was given by the monohydrate, which is the metastable phase at this temperature also, and the lower value by the anhydrous acid.

The dihydrate of sulphanilic acid, obtained by crystallisation from its solutions below 20°, is a highly efflorescent substance, and, if exposed to the air of the room, loses almost all its water in twelve hours, ultimately becoming anhydrous. The monohydrate, on the other hand, has on several occasions been similarly exposed, side by side with the watch-glass containing the dihydrate, without losing weight at all. In one experiment, indeed, the monohydrate retained its weight unchanged for over a fortnight, and even then showed no sign of losing water. This may be an instance of suspended transformation, but the comparative *rates* of dehydration of the two hydrates, obtained in other experiments, indicate that the process is different in the two cases.

A specimen of the monohydrate, kept in a closed vessel (a desiccator) over 49 per cent. sulphuric acid, lost weight slowly, and after two days still retained half its water of crystallisation. A specimen of the dihydrate, on the other hand, exposed in the same vessel, lost weight rapidly, as shown by the following record:

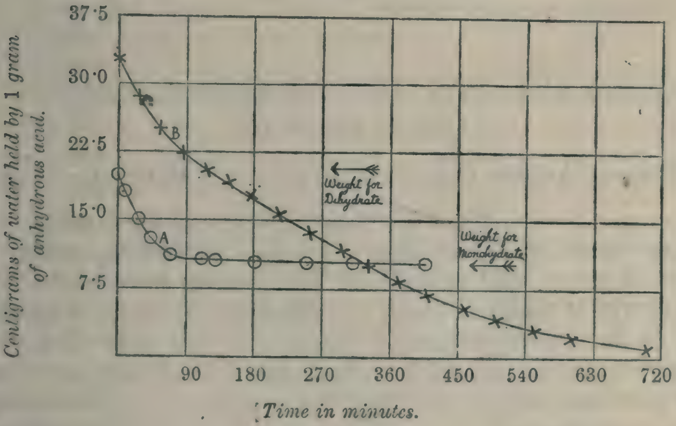
| Time of exposure. | Per cent. loss of weight. |
|---|---|
| 3·5 hours | 6·7 |
| 7·0 ,, | 13·3 |
| 22·5 ,, | 17·0 |
| After 3 hours further in a vacuum desiccator | 17·4 |

It will be seen that the dihydrate loses weight at a nearly uniform rate, whether its content of water is above or below that corresponding with the monohydrate. It is true that the rate of loss of weight becomes lower when dehydration is nearly complete, but the uniform rate persists until the point corresponding with the monohydrate is well passed.

The difference in the behaviour of monohydrate and dihydrate is clearly brought out by Fig. 2, in which two dehydration curves, similar to many others which have been recorded, are reproduced. Slightly moist crystals of the monohydrate were weighed out on a watch-glass, and this was kept all the time in the balance case, the air in which was partly dried by a few dishes containing concentrated sulphuric acid. Weighings made from time to time showed how the dehydration was proceeding. The curve *A*, obtained by plotting the weight of water (in centigrams) held by 1 gram of anhydrous acid at various times, shows that in the case of the monohydrate the mechanically held moisture comes off rapidly, and that when the composition has reached the point corresponding with a water content of 1 molecule per molecule of anhydrous acid, there is practically no further loss of weight under the conditions of the experiment. Curve *B* is a graphical reproduction of the corresponding record obtained with slightly moist crystals of dihydrate exposed to the same conditions. The chief features of curve *B* are the change of slope about the point corresponding with the dihydrate, and the absence of a break, or even a change of direction, at the point corresponding with the monohydrate. It is perhaps worth noting that the crystals, whether of monohydrate or dihydrate, employed in these experiments, had been filtered from their mother liquors and then transferred directly to the watch-glasses without grinding or further drying.

It has been suggested above that the absence of change in the monohydrate under certain conditions is probably due to suspended transformation. In connexion with this, a comparative experiment was made with two specimens of monohydrate derived from the same crystallisation, one of which, however, was finely ground, whilst the other was not so treated. On exposure to the air of the room, the untreated acid remained of constant weight, whilst the finely ground specimen lost weight slowly, much more slowly than unground dihydrate under similar conditions. Although, therefore, the state of division has undoubtedly some influence on the progress of dehydration, this factor cannot adequately account for the very different rates of dehydration observed for the two hydrates.

FIG. 2.



With the object of ascertaining the dissociation pressures of the two hydrates, specimens of each were exposed in closed vessels (desiccators) containing sulphuric acid of various strengths. It was found that the monohydrate lost weight slowly over 35·4 per cent.

acid (aqueous vapour pressure about 11·6 mm. at 20°), but retained its weight unaltered over 30·9 per cent. acid (aqueous vapour pressure about 12·9 mm. at 20°). The dihydrate lost weight slowly over 14·9 per cent. acid (aqueous vapour pressure about 16·5 mm. at 20°), but showed no loss over 9·4 per cent. acid (aqueous vapour pressure about 16·9 mm. at 20°).

The author desires to express his thanks to Mr. H. R. Courtman and Mr. E. Jobling, who assisted in the preliminary stages of this investigation.

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# XXXVI.—*The Alkaloids of* Xanthoxylum brachyacanthum.

By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN.

THE genus *Xanthoxylum* (or *Zanthoxylum*) of the natural order Rutaceæ contains some eighty species, distributed chiefly over Africa, America, and Australia. Perhaps the best known is the Prickly Ash of North America (*X. americanum*), which is an official drug of the United States Pharmacopœia. In spite of the large number of species available, few chemical examinations of these trees have been carried out, but those results which were obtained before 1889 are dealt with in detail in the introduction to Giacosa and Soave's paper (*Gazzetta*, 1889, **19**, 303) on *X. senegalense*, and there have been few since then.

For our purpose it will be sufficient to mention that although the presence of alkaloids in several species of *Xanthoxylum* has been recorded, and in particular the presence of berberine has been suspected, in no case has an alkaloidal constituent been characterised definitely, much less identified. Only in two cases have the alkaloids of a *Xanthoxylum* received more than superficial attention.

The alkaloids of *X. senegalense* (artar root) have been investigated by Giacosa and Soave (*loc. cit.*). These authors isolated two alkaloids, the principal of which they called artarine; it formed a rose-grey, amorphous mass, yielding yellow, crystalline salts, which gave on analysis figures equally in agreement for derivatives of the two formulæ, $C_{21}H_{23}O_4N$ and $C_{20}H_{17}O_4N$; the second base, which was not analysed, formed blood-red needles and gave yellow salts.

Two alkaloids, α- and β-xantherine, have recently been isolated from *X. ochroxylum* by Leprince (*Bull. Sci. Pharmacol.*, 1911, **18**, 337). The first has the formula $C_{24}H_{23}O_6N$, but no formula is given for the second; both yield yellow salts. The properties of all these alkaloids are entirely different from those of the alkaloids of *X. brachyacanthum* now described.

The material used for the present investigation was kindly supplied to us by the authorities of the Imperial Institute, and represented the bark of *X. brachyacanthum* obtained from Queensland, Australia. A specimen was submitted to the authorities at Kew, who reported that it had the same type of structure as the bark of specimens of *Xanthoxylum brachyacanthum*, F. Muell, in the museum at Kew, and that it probably belonged to this species or some other species of *Xanthoxylum.*

*Xanthoxylum brachyacanthum* has not previously been the subject of a chemical examination. The physiological properties of a tincture of the bark were, however, described to the Therapeutic Society by Dr. J. Gordon Sharp in 1906; these properties are not in accord with those observed by our collaborator, Dr. P. P. Laidlaw, for the pure alkaloids which we have isolated.

Preliminary examination showed that the bark contained a large amount of alkaloid which was readily extracted by dilute acids. When the extract was rendered alkaline with sodium carbonate or sodium hydroxide, however, only a very small amount of alkaloid was removed by extraction with chloroform, and it was, therefore, found necessary to employ a special method, which is described in the experimental part of this paper. It was then found that an alkaloid which was obtained in the form of its chloride,

$$C_{21}H_{24}O_4NCl,H_2O,$$

was present in large amount (1·85 per cent.), together with a small quantity (0·06 per cent.) of a second base having the composition $C_{21}H_{23}O_5N,\frac{1}{2}EtOH$.

The chloride of the alkaloid present in large amount melted at 262° (corr.), and the corresponding iodide, $C_{21}H_{24}O_4NI$, melted at 220° (corr.). This alkaloid contained two methoxyl groups, and one *N*-methyl group; it also contained a methylenedioxy-group, since it gave a positive result when Gaebel's test (*Arch. Pharm.*, 1910, **248**, 226) was applied. The chloride after drying had $[\alpha]_D -137·0°$.

The chloride was not decomposed by sodium hydroxide, and after treatment with silver hydroxide gave a very strongly alkaline aqueous solution, which on evaporation deposited an unsaturated anhydro-base, $C_{21}H_{23}O_4N$, which melted at 111—112° (corr.).

This chief alkaloidal constituent of the bark was thus shown to be a quaternary base, and its composition and properties suggested that it might be one of the two possible varieties of *l*-canadine (*l*-tetrahydroberberine) methochloride.

The methochlorides of *l*-canadine have not previously been described, but E. Schmidt (*Arch. Pharm.*, 1894, **232**, 136) has given the melting point of *l*-canadine methiodide as 228—232°. The recent work of Voss and Gadamer (*Arch. Pharm.*, 1910, **248**, 43), however, rendered it probable that Schmidt's methiodide was a mixture, for these authors have shown that *l*-canadine combines with ethyl iodide to form a mixture of the α- and β-ethiodides, the isomerism of which is due to the asymmetry of the nitrogen atom. They separated the two salts by crystallisation, then preparing from them the corresponding methochlorides, and characterised the salts with the following results:

l-*Canadine Ethyl Salts* (Voss and Gadamer).

| | M. p. | $[\alpha]_D$. |
|---|---|---|
| α-Ethochloride, $C_{22}H_{26}O_4NCl,2H_2O$ ......... | 233° | −127·3° |
| β-Ethochloride, $C_{22}H_{26}O_4NCl,2H_2O$ ...... | 245 | −138·3 |
| α-Ethiodide, $C_{22}H_{26}O_4NI,1\frac{1}{2}H_2O$ ........... | 187 | −91·5 |
| β-Ethiodide, $C_{22}H_{26}O_4NI$ ..................... | 225 | −115·3 |

They further showed that the α-variety could be converted into the β-form by the action of heat, as in the case of certain dialkylconiinium iodides containing both an asymmetric carbon atom and an asymmetric nitrogen atom which had been studied by Scholz (*Ber.*, 1905, **38**, 595). Similarly, McDavid, Perkin, and Robinson (T., 1912, **101**, 1218) obtained two isomeric tetrahydroberberine benzyl chlorides by the action of benzyl chloride on tetrahydroberberine. With the object, therefore, of identifying the alkaloid from *Xanthoxylum brachyacanthum*, we have investigated the action of methyl iodide on *l*-canadine. The methiodide produced crystallised in two forms, which appeared to separate simultaneously when either water or alcohol was employed as the solvent. The mixture was, therefore, converted into the methochlorides, which fortunately proved to have an entirely diverse solubility in water, and the sparingly soluble form—the β-variety—was readily obtained in a pure state by recrystallisation from this solvent. The mother liquor when evaporated to dryness and crystallised from absolute alcohol then deposited the α-methochloride, which was purified by recrystallisation from absolute alcohol. The corresponding α- and β-methiodides were then prepared from the pure methochlorides by double decomposition with potassium iodide, and recrystallisation from water. The properties of the salts were then found to be as follows:

### l-*Canadine Methyl Salts.*

| | M. p. | $[\alpha]_D$*. |
|---|---|---|
| α-Methochloride, $C_{21}H_{24}O_4NCl,H_2O$ ............ | 262° (corr.) | −136·4° |
| β-Methochloride, $C_{21}H_{24}O_4NCl,6H_2O$ ......... | 262 ,, | −160·9 |
| α-Methiodide, $C_{21}H_{24}O_4NI$ ......................... | 220 ,, | — |
| β-Methiodide, $C_{21}H_{24}O_4NI$ ......................... | 264 ,, | — |

* Of the anhydrous salts.

The methiodide of lower melting point passed into the variety of higher melting point when heated above its melting point, and is, therefore, termed the α-variety in accordance with the usage of Scholtz (*loc. cit.*).

The properties of the α-methyl salts of *l*-canadine agree with those of the quaternary alkaloid from *Xanthoxylum brachyacanthum*, and mixed melting-point determinations of the methochloride and methiodide confirmed the identity of the salts from either source. The quaternary chloride isolated from *Xanthoxylum brachyacanthum* is, therefore, *l*-α-canadine methochloride.

This is the first record, so far as we are aware, of the isolation from a plant of a substance containing an asymmetric nitrogen atom.

The physiological examination of the α- and β-methochlorides of *l*-canadine gave an interesting result. It is, of course, well known that the stereochemical configuration of substances containing an asymmetric carbon atom often profoundly effects their physiological action, as, for examples, hyoscyamine, adrenine, and pilocarpine. Very little is known, however, of the relative physiological behaviour of compounds the stereoisomerism of which is due to the asymmetry of a nitrogen atom. The only instance hitherto recorded in the literature is that of the dialkylconiinium iodides. Scholtz (*loc. cit.*) states on the authority of Hildebrandt that here the α-salts were less toxic than the β-salts; thus the doses of α- and β-ethylbenzylconiinium iodides which were just sufficient to cause paralytic curare-like action in medium-sized frogs were 2·6 and 1·5 milligrams respectively; in the cases of propylbenzyl- and butylbenzylconiinium iodides, smaller differences were observed. We were consequently interested to know whether differences in the physiological action of the α- and β-methochlorides of *l*-canadine were also to be observed. Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, kindly examined these salts, and found a very considerable quantitative difference in their physiological action.

On the frog neither substance caused local or general anæsthesia, but a gradual paralysis of all voluntary muscle developed, similar to that produced by curare and ammonium bases generally. *l*-β-Canadine methochloride was found to be much more active than the α-form in this respect. On the intact frog 1 milligram of the β-compound produced complete paralysis of all voluntary muscle in twelve minutes; 0·25 milligram failed to produce complete paralysis, but the frog was profoundly affected; 2·5 milligrams of the α-salt produced severe symptoms without producing complete paralysis.

The two salts were then compared by perfusing the hind limbs of frogs with dilutions of various strengths, and determining the rate at which paralysis of the nerve endings was produced.

In this set of experiments 1/10,000 and 1/20,000 of the α-salt were found to be almost exactly equal to 1/100,000 and 1/200,000 of the β-salt respectively. It is clear, then, that in their power of producing typical curare effect the β-salt is ten times as powerful as the α-one. As, however, in the above experiments the air-dried salts were employed, the 10:1 proportion does not really represent the relationship of the molecular activities correctly. Allowing for the fact that the α-salt crystallises with one molecule of water of crystallisation, and the β-salt with six molecules, a ratio of 12 to 1 is obtained.

On the mammal again these two alkaloids have actions very similar to those of curare. They cause large falls of blood pressure, and paralyse the ganglion cells of the vagus nerve. They produce paralysis of the respiratory centre in toxic doses. Both have a mild stimulating effect on the isolated uterus of a guinea-pig. In these various actions *l*-β-canadine methochloride is very obviously more active than the corresponding α-compound, but the ratio of activity between the two forms was only determined for their paralytic effect on frog muscle.

The second alkaloid of *Xanthoxylum brachyacanthum*, the base $C_{21}H_{23}O_5N,\frac{1}{2}EtOH$, which occurred only in small amount, melted at 170—171° (corr.) after drying at 100°. It was optically inactive, contained two methoxy-groups, one *N*-methyl group, and a methylenedioxy-group. Its hydrochloride and aurichloride were also obtained in crystalline form. Its chemical and physiological properties agree closely with those given for γ-homochelidonine, and there can be no doubt as to its identity with this alkaloid.

β- and γ-Homochelidonine, which are different but interconvertible forms of the same alkaloid, have already been isolated from *Chelidonium majus*, *Sanguinaria canadensis*, and *Eschscholtzia californica* by E. Schmidt and his collaborators, and from *Bucconia cordata* by Müller and Schlotterbeck and by Hopfgarten. The main features of the physiological action of this alkaloid are described by E. Schmidt (*Arch. Pharm.*, 1893, **231**, 143) on the authority of H. Meyer.

## EXPERIMENTAL.

### *Isolation of the Alkaloids of* Xanthoxylum brachyacanthum.

The crushed bark (8·7 kilograms) was percolated with 0·25 per cent. aqueous tartaric acid until no more alkaloid was removed. The percolate was then somewhat concentrated, filtered, and precipitated with aqueous mercuric chloride solution. The precipitated mercuric chlorides were then collected, washed with water, and decomposed by hydrogen sulphide in aqueous suspension. After filtering from mercuric sulphide the liquor was evaporated to low bulk, made alkaline with sodium hydroxide, and extracted many times with chloroform (mother liquor = M.1).

The chloroform extract was evaporated to dryness and extracted with very dilute hydrochloric acid; the acid extract after filtering was rendered alkaline with sodium carbonate, and completely extracted with ether, which on distillation left about 7 grams of crude γ-homochelidonine (p. 299) as a viscous oil, which soon crystallised.

The aqueous mother liquor was then mixed with sodium hydroxide and extracted with chloroform (mother liquor = M.2). The residue left on evaporation of the chloroform was mixed with acetone, and gave 93 grams of crude *l*-α-canadine methochloride as a buff-coloured, crystalline powder, melting at 250°.

This yield amounts to 1·07 per cent. of the bark, but does not represent the whole amount of this alkaloid present, since the mother liquors M.1 and M.2 still contained further quantities, which were not, however, isolated in this experiment. In a separate, small, completed extraction with 500 grams of bark, 9·25 grams of crude, crystalline *l*-α-canadine methochloride were isolated, that is, 1·85 per cent. of the bark.

### l-α-*Canadine Methochloride from* Xanthoxylum brachyacanthum.

The crude product isolated as previously described was crystallised, first from strong and then several times from absolute alcohol, when it was obtained in colourless, prismatic needles, which melted and decomposed at 262° (corr.). The mother liquors from this salt were evaporated to remove alcohol, dissolved in water, and precipitated as iodide by the addition of potassium iodide. After crystallisation from water, using animal charcoal, most of the remaining quantity of the alkaloid was recovered as *l*-α-canadine methiodide melting at 220° (corr.).

l-*α-Canadine methochloride* prepared as above crystallises with $1H_2O$. It is very readily soluble in water or hot alcohol, and easily so in cold alcohol, but insoluble in acetone:

0·1902 * gave 0·4341 $CO_2$ and 0·1094 $H_2O$. C=62·2; H=6·4.
0·6285 * lost 0·0257 at 100°. $H_2O$=4·1.
$C_{21}H_{24}O_4NCl,H_2O$ requires C=61·8; H=6·4; $H_2O$=4·4 per cent.
0·0932 † gave 0·2199 $CO_2$ and 0·0545 $H_2O$. C=64·3; H=6·5.
0·1494 † „ 0·0530 AgCl. Cl=8·8.
$C_{21}H_{24}O_4NCl$ requires C=64·7; H=6·2; Cl=9·1 per cent.

A determination of the specific rotatory power of the anhydrous salt in aqueous solution gave the following result:

$$\alpha_D\ -11{\cdot}50°;\ c=4{\cdot}197;\ l=2;\ [\alpha]_D\ -137{\cdot}0°.$$

l-*α-Canadine methiodide* crystallises from water in prisms which melt at 220° (corr.) when fairly rapidly heated. When kept at this temperature for a few seconds the molten mass begins to crystallise, and then does not melt and decompose until about 250° (corr.).

*l*-*α*-Canadine methiodide is very sparingly soluble in cold, and sparingly so in boiling water. It is anhydrous:

0·1708 gave 0·3282 $CO_2$ and 0·0746 $H_2O$. C=52·4; H=4·9.
0·3744 ‡ „ 0·3686 AgI at 180—200°. OMe=13·0:
and 0·1692 AgI at 300—330°. NMe=5·6.
$C_{21}H_{24}O_4NI$ requires C=52·4; H=5·0; $(OMe)_2$=12·7;
NMe=6·0 per cent.

### *Methylation of* l-*Canadine. Formation of the α- and β-Methochlorides.*

*l*-Canadine readily combines with methyl iodide when gently warmed on the water-bath, but the resulting mixture of the methiodides could not be readily separated by fractional crystallisation either from water or alcohol. It was found, however, that the solubilities of the methochlorides in water were somewhat widely apart, and the two isomerides were obtained in a pure state by means of the following process.

Thirty grams of natural *l*-canadine, which melted at 133—134° (corr.) and had $[\alpha]_D$ −299° ($c$=1·3264), were boiled under a reflux condenser for half an hour with 45 c.c. of methyl iodide and 30 c.c. of methyl alcohol. The solvents were then distilled off, and the resulting mixture of *l*-*α*- and *l*-*β*-canadine methiodides dissolved in 1·5 litres of boiling water. This solution was digested with an excess of silver chloride, filtered from the silver salts, and the resulting solution of *l*-*α*- and *l*-*β*-canadine methochlorides evaporated to a thin syrup and set aside to crystallise. The somewhat sparingly soluble *l*-β-canadine methochloride then separated in large, hard prisms, which were purified by recrystallisation from water. The mother liquor on concentration gave a further small quantity, and 21·2 grams of the pure salt were thus obtained; this yield represents 48 per cent. of the theoretical.

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* Air dried. † Dried at 100°.
‡ By Zeisel's and Herzig and Meyer's methods.

The syrupy mother liquor from which *l*-β-canadine methochloride had been thus removed was evaporated to dryness in a vacuum, and dissolved in about 10 c.c. of absolute alcohol, when on keeping, a small quantity of *l*-α-canadine methochloride separated. The mother liquors from this were again evaporated to dryness and dissolved in absolute alcohol, when a further quantity of the same salt was obtained. The two crops were then combined and recrystallised from absolute alcohol, when 4·5 grams of pure *l*-α-canadine methochloride were obtained. This salt melted at 260° (corr.) alone and when mixed with the salt derived from *Xanthoxylum brachyacanthum*; it had $[\alpha]_D$ −136·4° ($c = 3·7264$). A specimen of the α-methiodide prepared from it by precipitation with potassium iodide and recrystallisation from water, melted at 220° (corr.) alone or when mixed with *l*-α-canadine methiodide from *Xanthoxylum brachyacanthum*, and like the latter salt solidified just above its melting point and did not then decompose until about 250° (corr.).

The yield of *l*-α-canadine methochloride thus isolated, 4·5 grams, represents only 12 per cent. of the theoretical. There then remained a syrup which after the complete removal of the alcohol and slight dilution with water deposited a further small quantity of the β-methochloride. The syrup obviously represented a mixture of the α- and β-salts, and was not worked up further.

l-β-*Canadine methochloride* crystallises from water in large, colourless, oblong prisms containing $6H_2O$, of which 5 are lost at 100°. The air-dried salt partly melts in its water of crystallisation below 100°, starting to sinter at about 75°. After thorough drying at 100°, the salt when heated slowly loses the remaining molecule of water at about 200° with slight effervescence, and does not then melt until 262° (corr.). If heated quickly, the salt which has been dried at 100° may melt at about 200°. *l*-β-Canadine methochloride is somewhat sparingly soluble in cold water, but very readily so in hot water:

0·9958 air-dried salt lost 0·1854 at 100°. $H_2O = 18·6$.

$C_{21}H_{24}O_4NCl,6H_2O$ requires loss of $5H_2O = 18·1$ per cent.

0·1676 * gave 0·3822 $CO_2$ and 0·0962 $H_2O$. $C = 62·2$; $H = 6·4$.

0·1993 * „ 0·4528 $CO_2$ and 0·1112 $H_2O$. $C = 61·9$; $H = 6·2$.

$C_{21}H_{24}O_4NCl,H_2O$ requires $C = 61·8$; $H = 6·4$ per cent.

* Dried at 100°.

A determination of the specific rotatory power in aqueous solution gave the following result:

$\alpha_D$ $-9{\cdot}94°$; $c = 3{\cdot}233$ of salt dried at 100°; $l = 2$; $[\alpha]_D$ $-153{\cdot}8°$, for the monohydrate, which is equivalent to $[\alpha]_D$ $-160{\cdot}9°$ for the anhydrous salt.

l-β-*Canadine methiodide* was prepared from the methochloride by double decomposition with potassium iodide. After crystallisation from hot water it formed small prisms, which decomposed at 264° (corr.). This salt is anhydrous, and is very sparingly soluble in water or alcohol:

0·1614 gave 0·3082 $CO_2$ and 0·0733 $H_2O$. C=52·1; H=5·1.

$C_{21}H_{24}O_4NI$ requires C=52·4; H=5·0 per cent.

### *Conversion of the α- into the β-Form.*

It has already been stated that when *l*-α-canadine methiodide is heated above its melting point the liquid first formed becomes crystalline, and does not then melt until about 250°. In order to ascertain with certainty whether the resulting product was *l*-β-canadine methiodide or not, the following experiment was conducted.

A fraction of a gram of *l*-α-canadine methiodide was heated to 230°, and maintained at this temperature for about two minutes. The discoloured product was then dissolved in boiling water decolorised by means of sulphurous acid and animal charcoal, and well shaken with an excess of silver chloride. After filtering from the silver iodide and chloride, the aqueous solution was evaporated to low bulk, when a small quantity of *l*-β-canadine methochloride separated in the typical oblong, colourless prisms, which melted below 100° in the air-dried condition.

### *Preparation of an Anhydro-base from* l-*Canadine Methohaloids.*

Ten grams of *l*-α-canadine methiodide from *Xanthoxylum brachyacanthum* were dissolved in about 200 c.c. of boiling water, and digested with an excess of silver hydroxide until the solution was free from iodide. After filtering, the strongly alkaline solution of the methohydroxide was evaporated to dryness on the water-bath in an open dish, when an insoluble oil was formed. The residue was then mixed with 100 c.c. of water, and again evaporated to dryness. It was then extracted several times with small quantities of warm water, the extracts being decanted each time from the insoluble, amorphous residue. The latter was then covered with ether, when it immediately began to crystallise; after stirring with ether for a short time, the whole quantity became converted into crystals, which melted at 105—110°. After one crystallisation from alcohol, 4·1 grams of the anhydro-base were obtained. This base crystallises from alcohol in colourless clusters of needles, which melt at 111—112° (corr.). It is insoluble in water, somewhat sparingly soluble in cold alcohol, but readily so in hot alcohol. It is anhydrous. It behaves as an unsaturated compound towards bromine or permanganate:

0·1813 gave 0·4748 $CO_2$ and 0·1070 $H_2O$. C=71·6; H=6·6.

$C_{21}H_{23}O_4N$ requires C=71·4; H=6·6 per cent.

The specific rotatory power of the once crystallised base was $[\alpha]_D$ −25·2°, but this gradually diminished with successive crystallisations. A similar result was obtained starting from *l*-*β*-canadine methochloride, thus affording further confirmation of the identity of the salt from *Xanthoxylum brachyacanthum* with a methyl salt of *l*-canadine.

The optical behaviour of the anhydro-base is of particular interest in connexion with the study of the mechanism of the degradation of tetrahydroberberine by Hofmann's method, and it is proposed to continue the work in this direction.

### γ-*Homochelidonine from* Xanthoxylum brachyacanthum.

The crude product previously described (p. 295) was purified by crystallisation from alcohol, when 5·6 grams of the pure base were obtained in stout, colourless needles, which contained half a molecular proportion of alcohol of crystallisation and melted at 170—171° (corr.) after drying at 100°. It is insoluble in water, somewhat sparingly soluble in cold, readily so in hot, alcohol, sparingly so in ether, and readily so in chloroform.

Air-dried base:

Found: C=67·1; H=6·8. Loss at 130°=6·2.

$C_{21}H_{23}O_5N,\frac{1}{2}EtOH$ requires C=67·3; H=6·7; EtOH=5·9 per cent.

Base dried at 130°:

Found: C=68·2, 68·6; H=6·0, 5·7. M.W.=356, 360.

$C_{21}H_{23}O_5N$ requires C=68·3; H=6·3 per cent. M.W.=369.

This base is soluble in dilute acids, and is precipitated by alkali hydroxides, sodium carbonate, or ammonia, but is soluble in a large excess of the latter. It is optically inactive ($c$=2·137 in chloroform; $l$=2 dcm.). It neither couples nor forms a nitrosoamine when treated with nitrous acid, and is, therefore, a tertiary base.

It contains a methylenedioxy-group, for on applying Gaebel's test (*Arch. Pharm.*, 1910, **248**, 226) a clear red solution is obtained at once, and this becomes turbid when digested in the water-bath.

It contains two methoxyl and one $N$-$CH_3$ groups:

0·2014, dried at 130°, gave 0·2572 AgI at 160—180°. OMe = 16·9:
and 0·1174 AgI at 280—300°. NMe = 7·2.

$C_{21}H_{23}O_5N$ requires $(OMe)_2 = 16·8$; NMe = 7·9 per cent.

The hydrochloride, $C_{21}H_{23}O_5N,HCl,1\frac{1}{2}H_2O$, crystallises from water in colourless, microscopic needles, which have no sharp melting point, but after drying at 100° begin to turn yellow, and sinter at about 165° and effervesce at about 175° (corr.). This salt crystallises with $1\frac{1}{2}$ molecules of water of crystallisation, of which the molecule is lost at 100°. (Found, loss = 3·4. Calc., 4·2 per cent. Found, in dried salt, C = 60·3; H = 6·3; Cl = 8·7. Calc., C = 60·8; H = 6·1; Cl = 8·6 per cent.)

The aurichloride, $C_{21}H_{23}O_5N,HAuCl_4$, crystallises from alcohol in garnet-red grains, which decompose at 192° (corr.). It is anhydrous, and is very sparingly soluble in water or cold alcohol, but fairly readily so in hot alcohol. (Found, Au = 28·0. Calc., Au = 27·8 per cent.)

In conclusion, we wish to express our thanks to the Director of the Imperial Institute for suggesting the investigation of the bark, and for a supply of raw material.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

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# XXXVII.—*The Precipitation of Lead Thiosulphate and its Behaviour on Boiling with Water.*

By WILLIAM HUGHES PERKINS and ALBERT THEODORE KING.

THE formation of lead sulphide when lead thiosulphate is boiled with water is explained in several ways in modern works of reference. On the sole authority of Fogh (*Ann. Chim. Phys.*, 1890, [vi], **21**, 56) the reaction is frequently represented by means of the equation:

$$2PbS_2O_3 = PbS + PbS_3O_6.$$

The present authors, having failed to obtain lead trithionate by this reaction, have examined the data in Fogh's paper, and have come to the conclusion that the above equation has no justification. Apart from the fact that the lead thiosulphate used in the experiments was prepared by a method which probably gave an impure product, the actual experimental data are arithmetically untrustworthy. Starting with 5·087 grams of the thiosulphate, and boiling in a large quantity of water for three hours, Fogh obtained a precipitate which weighed 3·5160 grams, and a filtrate containing both lead and sulphur. On the basis of the above equation, 1·906 grams of sulphide and 3·181 grams of trithionate should be formed. After determining the total lead and total sulphur in both precipitate and filtrate, he expressed his results as follows: The calculated values are obtained from the assumption that the precipitate contains all the lead sulphide (1·906 grams) and 1·610 grams of the trithionate, the remaining trithionate, 1·571 grams, being in the filtrate.

| | Precipitate. | | Filtrate. | |
|---|---|---|---|---|
| | Calc. | Found. | Calc. | Found. |
| Lead .................. | 2·490 | 2·479 | 0·817 | 0·809 |
| Sulphur ............... | 0·646 | 0·638 | 0·213 | 0·209 |

On examining these figures it will be observed that the ratio of lead to sulphur in the filtrate does not correspond with that required for $PbS_3O_6$, and that, in fact, the calculated quantity of sulphur should be 0·379. This error is so remarkable that it seems reasonable to assume that Fogh calculated the amount of sulphur in 1·571 grams of lead sulphide, which is 0·211 gram. In view of the close agreement between the experimental and the wrongly calculated numbers, it is impossible to base any deduction on the analytical results, and the above equation is without quantitative support.

Another equation which is frequently used to describe the change is that suggested from analogy to the similar behaviour of the silver salt, namely, $PbS_2O_3 + H_2O = H_2SO_4 + PbS$. The authors have found that only a very slight acidity is developed on boiling for many hours, so that sulphuric acid cannot be assumed to be an essential final product of the reaction. Faktor (*Zeitsch. anal. Chem.*, 1900, **39**, 351) states that the precipitate produced by adding hot concentrated sodium thiosulphate to lead nitrate solution does not blacken, but only turns grey. In the presence of ammonium chloride, however, the blackening is rapid, and he asserts that the precipitate is then composed entirely of lead sulphide. Norton (*Chem. News*, 1901, **89**, 254), who heated lead thiosulphate with water in sealed vessels to over 140°, appears to be the only worker who has recognised the presence of considerable quantities of free sulphur in the black residue. Attention to this fact, together with the observation that the change takes place most readily in the presence of excess of sodium thiosulphate, has led the present authors to the conclusion that the ordinary reaction is best represented, as far as the initial and final states are concerned, by the equation:

$$PbS_2O_3 + 3Na_2S_2O_3 = PbS + 4S + 3Na_2SO_4.$$

This change may be due to the transformation of a complex ion in solution, because the indications are much less clear in the case of lead thiosulphate alone, although even in this case the products are sulphide sulphate, and free sulphur with small amounts of sulphuric acid, the main reaction being probably analogous to the above, that is, $4PbS_2O_3 = PbS + 4S + 3PbSO_4$. It will be seen that both these reactions bear a close resemblance to the usually accepted representation of the decomposition of sodium thiosulphate when heated alone in the absence of air, $4Na_2S_2O_3 = Na_2S + 4S + 3Na_2SO_4$.

The trustworthiness of Fogh's data is still more questionable when his method of preparing lead thiosulphate is considered. In the analysis of specimens prepared by precipitation from lead acetate the authors have found that the percentage of sulphur determined gravimetrically and the amount of thiosulphate determined iodometrically are almost invariably lower than those deduced from the formula $PbS_2O_3$, and that the discrepancy is caused by the presence of lead acetate. From fairly concentrated solutions using equivalent quantities of lead acetate and sodium thiosulphate, the precipitate is the double salt,

$$Pb(C_2H_3O_2)_2,2PbS_2O_3,$$

which has previously been obtained in a less direct manner by Lemoult (*Compt. rend.*, 1904, **139**, 422). From more dilute solutions or in the presence of excess of sodium thiosulphate, the precipitate approximates more closely to the simple salt, $PbS_2O_3$, but once the double salt has been precipitated it is remarkably stable, and requires prolonged washing with water to effect any change in its composition. For this reason it is unlikely that Fogh, who mixed $N/2$-solutions of lead acetate and sodium thiosulphate,* and did not presumably take any excessive precautions in washing, obtained a precipitate containing 20·1 per cent. of sulphur, which is the theoretical figure for $PbS_2O_3$, and the analytical value given in his paper. It must be noted that the percentage of lead is of little value in distinguishing between the two salts, since:

$PbS_2O_3$ requires Pb = 64·85; S = 20·10.
$Pb(C_2H_3O_2)_2,2PbS_2O_3$ requires Pb = 64·46; S = 13·32 per cent.

Fogh states that from $N/2$-solutions he obtained a filtrate containing only sodium acetate and a precipitate, which contained, after washing, 20·1 per cent. of sulphur. The authors obtained a filtrate containing a considerable quantity of thiosulphate and a precipitate with less than 17 per cent. of sulphur. The exact nature of the equilibrium between lead acetate, sodium thiosulphate, and water is being made the subject of further inquiry, but it is safe to conclude that the thermochemical and other data and conclusions of Fogh, based on the assumption that his precipitate was pure thiosulphate, are not correct. In the present investigation all specimens of lead thiosulphate for the study of its decomposition were obtained from the nitrate by adding an equivalent quantity of sodium thiosulphate, a process which is found to yield the pure salt.

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* For this purpose a $N$-solution of sodium thiosulphate contains half a gram-molecule per litre. It is, of course, only $N/2$ referred to iodine.

## EXPERIMENTAL.

*The Precipitation of Lead Thiosulphate.*—12·5 Grams of sodium thiosulphate and 19·0 grams of lead acetate (equivalent quantities) were each dissolved in about 150 c.c. of water, and the solutions mixed. The resulting precipitate was washed by decantation several times, collected, and dried in a vacuum desiccator. It was first analysed by oxidising with bromine, removing the lead sulphate, and then treating the filtrate with barium chloride to obtain the rest of the sulphur as barium sulphate. Owing to the amount of hydrobromic acid produced in the oxidation, the lead is not all precipitated as sulphate, so that the results for lead may be expected to be rather low. As the mean of several analyses we obtained Pb = 63·54; S = 13·33 per cent. The precipitate is obviously not pure lead thiosulphate (S = 20·10 per cent.), but corresponds closely with $Pb(C_2H_3O_2)_2,2PbS_2O_3$, which only requires 13·32 per cent. of sulphur. As a check on this analysis the iodometric method of Lemoult (*loc. cit.*) was used. The precipitate was dissolved in concentrated potassium hydroxide, the solution diluted, neutralised with sulphuric acid, using phenolphthalein as indicator, and finally titrated with $N/10$-iodine. In this way it was found that 1 gram of precipitate required 20·5, 20·4, and 20·5 c.c. of $N/10$-iodine (S = 13·1 per cent.). The pure thiosulphate requires 31·3 c.c., and the double salt 20·8 c.c. A specimen of thiosulphate precipitated in a similar manner from lead nitrate gave Pb = 64·50 and S = 20·32 per cent., and 1 gram required 30·8, 31·0, and 30·7 c.c. of $N/10$-iodine. In this case the product is practically pure lead thiosulphate. On repeating the precipitation from lead acetate, using very dilute solutions ($N/50$), the precipitation was much slower, and the product, which separated in a crystalline form, gave analytical data which showed that it was nearly pure thiosulphate. One gram required 30·6 c.c. of $N/10$-iodine (S = 19·6 per cent.). A few experiments were carried out to determine the effect of the concentrations of the reacting solutions, with equivalent quantities and with excess of sodium thiosulphate. As a result, it may be stated that the double salt is precipitated almost pure when solutions more concentrated than about $N/3$ are mixed in equivalent quantities, but that with excess of sodium thiosulphate the tendency to form the double salt is greatly diminished. The double salt, once precipitated, however, is not rapidly decomposed by washing with water, as the following experiment shows. The solutions are of the same concentration as those used by Fogh, although there is no indication that he washed his precipitate so thoroughly. 12·5 Grams of sodium thiosulphate and 19 grams of lead acetate were each dissolved in 200 c.c. of water ($N/2$-solutions), mixed, and well stirred. The precipitate settled quickly, and the clear liquid, which still contained a great deal of thiosulphate, was poured off and replaced by 300 c.c. of water. This was left in contact with the precipitate for an hour, being stirred repeatedly. This process was repeated five times, and after filtering, the precipitate was dried as before. On analysis 1 gram was found to require 26·2 c.c. of $N/10$-iodine (S=16·8 per cent.), that is, it still contains about one-sixth its weight of lead acetate.

In another experiment 3·841 grams of lead thiosulphate prepared from the nitrate were shaken with about 50 c.c. of $N$-lead acetate solution. After filtering and drying, the precipitate was found to weigh 5·634 grams, and 1 gram required 20·8 c.c. of $N/10$-iodine (S=13·3 per cent.). Complete formation of the double salt would have been accompanied by an increase in weight to 5·797 grams. The difference is partly due to the appreciable solubility of the double salt.

A corresponding double salt was prepared from lead butyrate by treating a concentrated solution with sodium thiosulphate. The analytical data given by this preparation were:

0·5438 gave 0·4688 $PbSO_4$. Pb=58·9.

0·5715 required 11·35 c.c. of $N/10$-iodine.

$Pb(C_4H_7O_2)_2,2PbS_2O_3$ requires Pb=60·94 per cent. and 11·2 c.c.

With lead trichloroacetate there appears to be little or no tendency to the formation of a double salt, as the following figures show:

4·140 Grams of anhydrous lead trichloroacetate (3 mols.) were dissolved in a small quantity of water, and 8·36 c.c. of 1·04$N$-sodium thiosulphate (2 mols.) of sodium thiosulphate were added. After allowing to remain, filtering, and washing with a little water the filtrate contained much lead and only a little thiosulphate. The whole of the filtrate required 1·0 c.c. of $N/10$-iodine, and gave

0·6838 gram of lead sulphate. This corresponds with 1·408 grams of lead trichloroacetate, whereas the amount added in excess of that required for the simple salt was 1·380 grams. 0·2338 Grams of precipitate required 7·30 c.c. of *N*/10-iodine, that is, 1 gram requires 31·2 c.c. (S = 20·0 per cent.), corresponding with pure lead thiosulphate.

A precipitate obtained by treating a hot saturated solution of lead formate with one-third of an equivalent of sodium thiosulphate, and rapidly cooling, was pure white, and 0·2301 gram required 7·02 c.c. of *N*/10-iodine, that is, 1 gram requires 30·5 c.c. (S = 19·6 per cent.), again obviously pure lead thiosulphate. Apparently only the weak acids which are chemically similar to acetic acid exhibit similar behaviour in this respect.

*The Boiling of Lead Thiosulphate with Water.*—In an attempt to repeat Fogh's experiment, 5·002 grams of the thiosulphate were boiled with 600 c.c. of water for four hours. A lead acetate paper held in the steam was very slowly blackened, showing that traces of hydrogen sulphide were evolved. After filtering, the filtrate was made up to a litre, and was found to be only slightly acid (100 c.c. required less than 1 c.c. of *N*/10-alkali), and to contain only very little undecomposed thiosulphate (100 c.c. required only 0·35 c.c. of *N*/10-iodine). Determinations of lead and sulphur were made in the filtrate, and the dried precipitate was extracted with pure carbon disulphide for the determination of free sulphur. The extracted residue was not found to contain more than small amounts of thiosulphate or of any thionic acid, but was almost entirely composed of sulphide and sulphate. The results of this and other similar experiments are summarised in the following table:

| | | | |
|---|---|---|---|
| Weight of thiosulphate taken | 5·002 | 4·578 | 2·377 |
| Lead contained (calculated) | 3·247 | 2·971 | 1·542 |
| Sulphur ,, ,, | 1·003 | 0·920 | 0·476 |
| Weight of residue | 4·441 | 4·163 | 2·113 |
| Free sulphur in residue | 0·316 | 0·277 | 0·125 |
| Combined sulphur in residue | — | 0·463 | — |
| Lead in residue | 2·999 | 2·855 | 1·421 |
| Sulphur in filtrate | 0·172 | 0·137 | 0·108 |
| Lead ,, ,, | 0·198 | 0·155 | 0·103 |
| Total sulphur found | 0·953* | 0·877 | 0·453* |
| ,, lead ,, | 3·197 | 2·970 | 1·524 |

* Assuming the atomic ratio S : Pb in the extracted residue = 1 : 1. In the other experiment this ratio is slightly exceeded.

From these figures it will be seen that the lead is almost completely converted into sulphide and sulphate, and that a considerable amount of free sulphur is liberated. The equation which suggests itself for such a change is $4PbS_2O_3 = 3PbSO_4 + PbS + 4S$, which requires, however, the liberation of half the sulphur in the free state. The deficiency in free and in total sulphur, and the large amount of sulphur in the filtrate, are not surprising considering the conditions of the experiment. Sulphur at 100° is appreciably volatile, and acts on water according to the equation $3H_2O + 4S = H_2S_2O_3 + 2H_2S$, or in the presence of oxygen: $3H_2O + 3S + O = H_2SO_4 + 2H_2S$ (Francis Jones, *Mem. Manchester Phil. Soc.*, 1912, **56**, No. XIV).

The excess of combined sulphur in the filtrate is accounted for by the presence of free acid and of polythionates. The filtrates in the above experiments required 16, 8, and 10 c.c. respectively of *N*/10-alkali for neutralisation. The addition of excess of sodium hydroxide produced in each case a slight turbidity of sulphur, and on keeping for some hours a precipitate of lead sulphide was deposited. Ammoniacal silver nitrate did not give an immediate precipitate, but in a few minutes the black precipitate characteristic of pentathionate was produced.

In order to obtain further information as to the nature of the change, lead thiosulphate or lead nitrate was heated with excess of sodium thiosulphate, when the blackening took place much more rapidly. A weighed quantity of the lead salt was dissolved in a concentrated solution of sodium thiosulphate of known concentration, and the solution sealed up in a glass tube. On warming for a few minutes in a steam-bath a copious, black precipitate was formed. It was first deposited as a mirror on the walls of the tube, and subsequently peeled off. A yellow cloud of sulphur could also be clearly seen. When the action had ceased, the tube was opened, and the precipitate collected. A slight odour of hydrogen sulphide was always observed on opening the tube, but the amount of sulphide in solution was practically negligible. The amount of thiosulphate in the filtrate was determined iodometrically, and the total sulphur present as thiosulphate and sulphate by oxidation with bromine and precipitation as barium sulphate. The free sulphur was extracted from the precipitate by means of carbon disulphide, the residue after this process being in all cases practically pure lead sulphide. In this way the following results were obtained:

1·3110 Grams of lead thiosulphate were heated with 20·0 c.c. of 0·990*N*-sodium thiosulphate. The filtrate after opening the tube was made up to 250 c.c. The precipitate was collected in a tared Gooch crucible, and dried in a desiccator. It weighed 1·506 grams. Twenty-five c.c. of the filtrate required 7·70 c.c. of *N*/10-iodine, so that 121 c.c. of *N*/10-sodium thiosulphate had been consumed. This represents 2·92 molecules for each molecule of lead thiosulphate. The weight of sulphur extracted was 0·520 gram, which is equivalent to 3·96 atoms. The residue after extraction, 0·986 gram, corresponds with 1·00 molecule of lead sulphide. These figures agree remarkably well with the equation:

$$PbS_2O_3 + 3Na_2S_2O_3 = PbS + 4S + 3Na_2SO_4,$$

which also requires three molecules of sodium sulphate in the filtrate. On adding bromine to 25 c.c. of the filtrate and precipitating with barium chloride, the barium sulphate produced weighed 0·6452 gram. The 7·70 c.c. of sodium thiosulphate ($N/10$) account for 0·359 gram, so that there is in the filtrate a quantity of sodium sulphate corresponding with 2·86 grams of barium sulphate. This is 1·747 grams, equivalent to 2·99 molecules per molecule of lead thiosulphate originally taken. This and similar results are collected in the following table, the italics indicating the number of equivalent molecules or atoms of the substance per molecule of lead salt. It will be noted that the numbers obtained by the use of lead nitrate lead to a similar equation.

| Weight of lead salt. | C.c. $N$/10-thiosulphate consumed. | Sulphur formed. | Lead sulphide. | Sodium sulphate. |
|---|---|---|---|---|
| 1·3110 $PbS_2O_3$...... | 121·0 (*2·94*) | 0·520 (*3·96*) | 0·986 (*1·00*) | 1·747 (*2·99*) |
| 1·4533 $PbS_2O_3$...... | 130·5 (*2·86*) | 0·549 (*3·77*) | 1·077 (*0·99*) | 1·918 (*2·96*) |
| 1·0385 $PbS_2O_3$...... | 94·0 (*2·89*) | 0·394 (*3·78*) | 0·748 (*0·96*) | 1·353 (*2·93*) |
| 0·9987 $Pb(NO_3)_2$ .. | 116·0 (*3·84*) | 0·364 (*3·77*) | 0·709 (*0·99*) | 1·292 (*3·01*) |
| 1·0006 $Pb(NO_3)_2$ .. | 118·5 (*3·93*) | 0·370 (*3·82*) | 0·723 (*1·00*) | 1·301 (*3·03*) |

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# XXXVIII.—*Ionisation and the Law of Mass Action.*

By WILLIAM ROBERT BOUSFIELD, M.A., K.C.

THE accurate determination of the coefficient of ionisation, even in comparatively dilute solutions, is still a matter of considerable uncertainty. A decisive test as between the various ionisation formulæ which have been proposed is still lacking, and none of the formulæ for "strong" electrolytes has been shown to be in conformity with the principles of the law of mass action. In endeavouring to apply the law of mass action to aqueous solutions, even at moderate dilutions, we are face to face with a very complicated problem. There can be little doubt that there is a progressive hydration of the solute as dilution increases, and that the water itself is a complex substance the proportions of the constituents of which are affected by the nature and amount of the solute; thus, even at moderate dilutions, to apply the law of mass action, we must probably write down at least two reaction equations belonging to the water itself, and an unknown number of reaction equations expressing the action of the water on the solute in its various stages of hydration. In the region of the highest dilution, when progressive hydration has nearly run its course and has reduced the molecular varieties of the solvent to the fewest possible, and when the proportion of water is so great that its constituents may be regarded as having constant proportions, the mass action problem ought to be reduced to its simplest form. The primary object of the present paper is to determine what is the true ionisation law in the region of highest dilution, so that the fundamental distinction between "strong" and "weak" electrolytes may be clearly enunciated.

In 1902 it was for the first time pointed out (Bousfield and Lowry, *Proc. Roy. Soc.*, 1902, **71**, 48) that the temperature-conductivity curve for "water" practically coincided with the temperature-fluidity curve. The coincidence of the curves revealed the fact that over a very wide range the mobility of the conducting ions was almost exactly proportional to the fluidity, and therefore inversely proportional to the viscosity of the liquid. In 1905 it was pointed out (Bousfield and Lowry, *Phil. Trans.*, 1905, *A*, **204**, 291) that the true coefficient of ionisation for binary electrolytes with univalent ions should be:

$$\alpha = \frac{\lambda}{\lambda_\infty} \cdot \frac{u_\infty + v_\infty}{u + v},$$

where $\lambda$ is the equivalent conductivity and $u$ and $v$ are the true mobilities of the ions, that is, numbers proportional to their actual velocities through the solution under a given potential gradient at the given concentration. It follows that in order to get the true value of $\alpha$ we have to take into account the variation of mobility with dilution. Now the mobility, according to Stokes' Law, should vary, not only inversely as the viscosity of the solution, but also inversely as the radii of the ions, if they can be treated as spherical. It was suggested that as a nearer approximation to the value of $\alpha$ the expression:

$$\alpha = \frac{\lambda \eta}{\lambda_\infty},$$

should be taken, where $\eta$ is the viscosity of the solution expressed in terms of the viscosity of water as unity. This correction for the effect of viscosity on the mobility, however, leaves untouched the effect of changes of ionic size, and could not alone be expected to lead to an accurate ionisation formula. Recently endeavours have been made to obtain a further approximation to the true value of $\alpha$ by taking, instead of $\eta$, a fractional power of $\eta$ which is a little less than unity (see Washburn, *J. Amer. Chem. Soc.*, 1911, **33**, 1470). This suggestion leaves out of the account the important considerations which arise from the varying sizes of the ions, and is, in fact, founded on experimental data which ignore such changes. To place the whole correction for $\alpha$ on the viscosity no doubt enables the ionisation formulæ to be moulded in such a way as to give formulæ which are apparently correct over a longer range of dilution, but the theoretical value of the formulæ for elucidating the conditions of mass action and determining the true correction for $\alpha$ is destroyed by such modifications. We must endeavour to get, not an ionisation law which is empirically accurate over a long range, but one which is absolutely accurate in the limiting case of infinite dilution.

Starting, then, with the values of $\alpha$ which are yielded by the expression $\alpha=\lambda\eta/\lambda_{\infty}$, as our first approximation to the value of $\alpha$, we must endeavour to get the ionisation law for infinite dilution from the highest range of values in which accurate experimental figures are obtainable, without striving for a formula which comprises the lower range of dilution, where the corrections due to variations of ionic size become more serious. Accuracy in the lower range, whilst the mobility change due to variation of ionic size is uncorrected, will certainly lead us away from the true ionisation law.

Kohlrausch has furnished us with a wonderfully accurate series of conductivity measurements for a number of electrolytes, which go right up to a concentration of $m=0{\cdot}0001$. When, however, we proceed to use the figures for the highest concentration as our basis we are met with another difficulty. Kohlrausch, no doubt, used water of very great purity for his solutions, but the effect of the correction for the water conductivity is debatable, and in the necessary manipulation of the solution it is impossible to avoid some change in the conductivity of the water. For $m=0{\cdot}0001$ the conductivity of a potassium chloride solution is:

$$\kappa_{18}=0{\cdot}00001291.$$

The conductivity of the water used would be of the order:

$$\kappa_{18}=0{\cdot}000001.$$

An error of 10 per cent. in the water conductivity would therefore produce an error of 0·8 per cent. in the conductivity and in the value of $\alpha$. This would produce a much larger error in the value of $(1-\alpha)$, which is the only sensitive factor in ionisation formulæ at high dilution. The divergence of the highest values from the main curve is soon seen when results are plotted. The very high range of dilution where the conductivity of the water introduces obvious errors must therefore be avoided.

Taking both these matters into account, the range of dilution in which we must seek for an ionisation law which shall be accurate at infinite dilution lies between $N/200$ and $N/2000$. With accurate figures between these limits we can avoid the water error and extrapolate with great accuracy past the point where water impurities introduce errors, into the limiting region of "infinite dilution."

We shall illustrate the formulæ which it is desired to examine by the figures for potassium chloride. To give detailed figures for other electrolytes would enlarge this communication too much, and is unnecessary, since we are dealing only with principles. In a former paper (Bousfield, *Phil. Trans.*, 1906, *A*, **206**, 155) a proof was given that the van't Hoff dilution law was accurate in the limiting case of infinite dilution. An analogous but simpler proof may now be given. It is convenient in expressing this and other dilution laws to use $h$, the total number of molecules of water present for one mol. of solute, instead of $m$ or $V$; $h$ is, of course, proportional to $V$ at high dilution. The van't Hoff law thus modified becomes:

$$\frac{\alpha^{\frac{3}{2}}}{1-\alpha} = Kh^{\frac{1}{2}}.$$

For purposes of calculation we may write this as:

$$\tfrac{3}{2}\log\alpha - \log(1-\alpha) = \tfrac{1}{2}\log h - C.$$

To test this equation we will take the first approximation figures for the ionisation-coefficient, namely, $\alpha = \lambda\eta/\lambda_\infty$. These values of

*Van't Hoff's Law.*

TABLE I.

| $m$. | $\alpha = \lambda\eta/\lambda_\infty$. | $y = \frac{3}{2}\log\alpha - \log(1-\alpha)$. | $x = \log h$. | $\Delta y$. | $\Delta x$. | $\Delta y/\Delta x$. | $C$. |
|---|---|---|---|---|---|---|---|
| 0·0001 | 0·9921 | 2·09721 | 5·74374 | — | — | — | — |
| 0·0002 | 0·9898 | 1·98472 | 5·44271 | — | — | — | — |
| 0·0005 | 0·9847 | 1·80526 | 5·04477 | 0·14557 | 0·30103 | 0·4836 | 0·71712 |
| 0·001 | 0·9788 | 1·65969 | 4·74374 | 0·14283 | 0·30104 | 0·4745 | 0·71218 |
| 0·002 | 0·9709 | 1·51686 | 4·44270 | 0·18751 | 0·39796 | 0·4667 | 0·70449 |
| 0·005 | 0·9562 | 1·32935 | 4·04474 | 0·13482 | 0·30107 | 0·4478 | 0·69303 |
| 0·01 | 0·9410 | 1·19453 | 3·74367 | — | — | — | — |
| 0·02 | 0·9218 | 1·05375 | 3·44248 | — | — | — | — |
| 0·05 | 0·8891 | 0·87849 | 3·04419 | — | — | — | — |
| 0·1 | 0·8600 | 0·75562 | 2·74257 | — | — | — | — |
| 0·2 | 0·8276 | 0·64019 | 2·44037 | | | | — |

$\alpha$ for potassium chloride, based on Kohlrausch's figures, are set out in the second column of table I. The third and fourth columns give the values of:

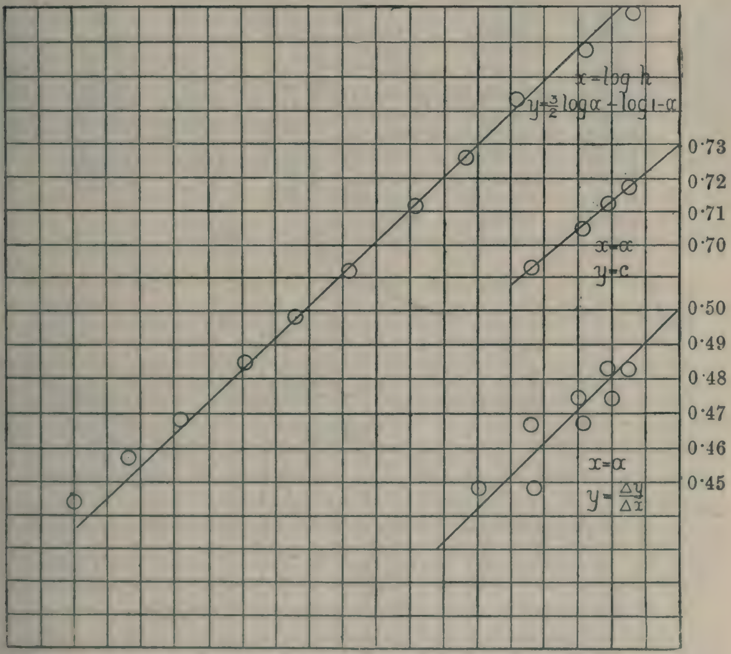
$$y = \tfrac{3}{2}\log\alpha - \log(1-\alpha)$$
$$x = \log h.$$

These values of $y$ and $x$ are set out in Fig. 1, which shows that the points from $m=0{\cdot}0005$ to $m=0{\cdot}005$ give approximately a straight line:

$$y=\tfrac{1}{2}x-C.$$

To determine the coefficient of $x$ exactly in the region of infinite dilution, the values of $\Delta y$ and $\Delta x$ are given in the table, and the values of $\Delta y/\Delta x$ are set out in the diagram on the values of $\alpha$ as abscissæ. They give approximately a straight line law, and show that the limiting value of $\Delta y/\Delta x$ is 0·5. It will be observed that each value of $\Delta y/\Delta x$ is set out twice on the two values of $\alpha$, one on each side of it. The true position, of course, lies somewhere between the two points, but they are so near as to leave no doubt that 0·5 is the true value of $\Delta y/\Delta x$ at infinite dilution. This is confirmed by taking the value $\frac{1}{2}$ for $\Delta y/\Delta x$ in order to determine what is the limiting value of the constant. For this purpose the values of $y-\frac{1}{2}x=-C$ are calculated and placed in the last column of the table. These are also set out in the diagram on the values of $\alpha$ as abscissæ, giving an excellent line, and showing that the value of $C$ at infinite dilution is 0·730.

FIG. 1.



By working from the values from $m=0{\cdot}0005$ to $m=0{\cdot}005$ we have been able to extrapolate to infinite dilution right past the values where the water error is serious, and we find that the equation which holds as we approach the limit is:

$$\tfrac{3}{2}\log\alpha - \log(1-\alpha) = \tfrac{1}{2}\log h - 0{\cdot}730,$$

which is the van't Hoff law.

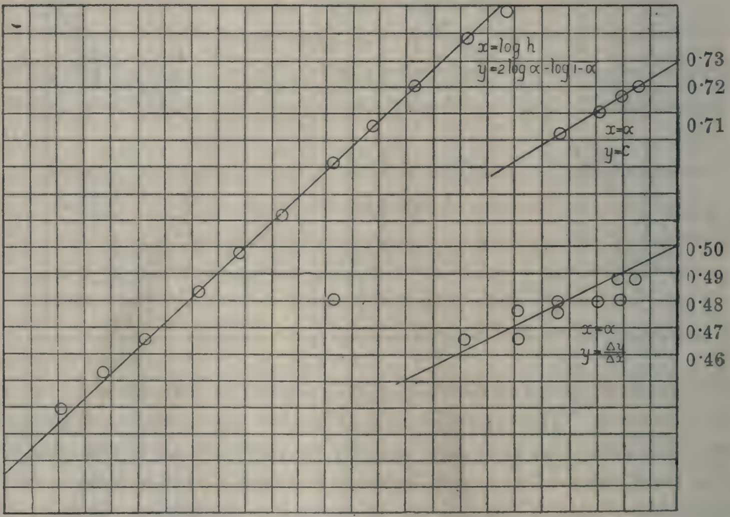
Let us now go through the same process for the Rudolphi law.

*Rudolphi's Law.*

TABLE II.

| $m$. | $\alpha=\lambda\eta/\lambda_\infty$. | $y=2\log\alpha - \log(1-\alpha)$. | $x=\log h$. | $\Delta y$. | $\Delta x$. | $\Delta y/\Delta x$. | $C$. |
|---|---|---|---|---|---|---|---|
| 0·0001 | 0·9921 | 2·09554 | 5·74374 | | | | — |
| 0·0002 | 0·9898 | 1·98250 | 5·44271 | — | — | — | — |
| 0·0005 | 0·9847 | 1·80191 | 5·04477 | — | — | — | 0·72047 |
| 0·001 | 0·9788 | 1·65504 | 4·74374 | 0·14687 | 0·30103 | 0·4879 | 0·71683 |
| 0·002 | 0·9709 | 1·51045 | 4·44270 | 0·14459 | 0·30104 | 0·4803 | 0·71090 |
| 0·005 | 0·9562 | 1·31963 | 4·04474 | 0·19082 | 0·39796 | 0·4795 | 0·70274 |
| 0·01 | 0·9410 | 1·17633 | 3·74367 | 0·14330 | 0·30107 | 0·4760 | — |
| 0·02 | 0·9218 | 1·03607 | 3·44248 | 0·14026 | 0·30119 | 0·4657 | — |
| 0·05 | 0·8891 | 0·85397 | 3·04419 | — | — | — | — |
| 0·1 | 0·8600 | 0·72287 | 2·74257 | — | — | — | — |
| 0·2 | 0·8276 | 0·59910 | 2·44037 | — | — | — | — |

FIG. 2.



The necessary figures are given in table II, and they are all set out in Fig. 2 as before. The same process is gone through, and the result is to give us the Rudolphi equation:

$$2\log\alpha - \log(1-\alpha) = \tfrac{1}{2}\log h - 0{\cdot}730.$$

We have then the apparently curious fact that both these equations are accurately true as we approach the limit of infinite dilution. The reason why they are both true is obviously because in the limit $\alpha = 1$, $\log \alpha = 0$, and therefore in the limit they both reduce to:

$$-\log(1-\alpha) = \tfrac{1}{2}\log h - 0{\cdot}730.$$

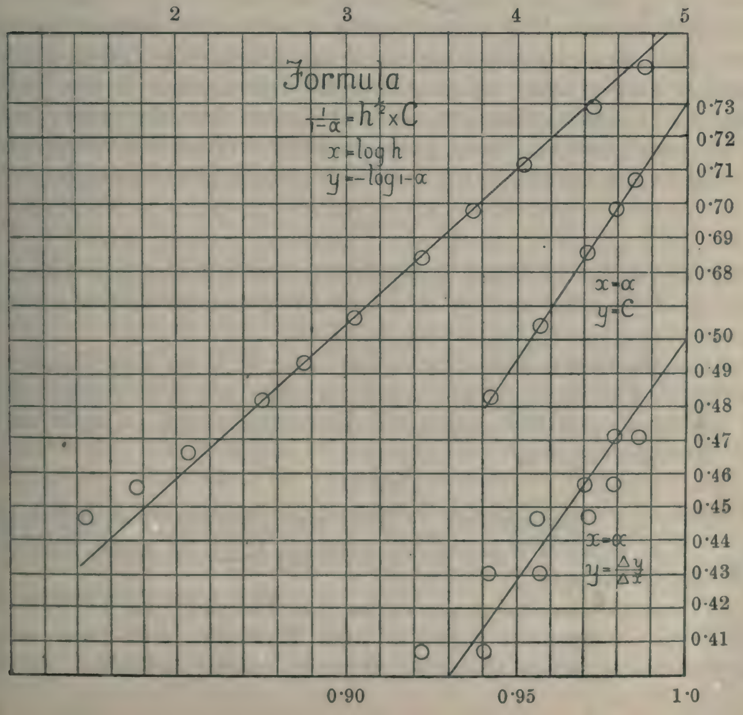
We will now test this new expression in the same way as the two preceding. The necessary figures are given in table III, and

TABLE III.

$$\frac{1}{1-\alpha} = h^{\frac{1}{2}} \times \text{Constant}.$$

| $m$. | $\alpha = \lambda\eta/\lambda_\infty$. | $y = -\log(1-\alpha)$. | $x = \log h$. | $\Delta y$. | $\Delta x$. | $\Delta y/\Delta x$. | $C$. |
|---|---|---|---|---|---|---|---|
| 0·0001 | 0·9921 | 2·10237 | 5·74374 | | | | — |
| 0·0002 | 0·9898 | 1·99140 | 5·44271 | — | — | — | — |
| 0·0005 | 0·9847 | 1·81531 | 5·04477 | — | — | — | 0·7071 |
| 0·001 | 0·9788 | 1·67366 | 4·74374 | 0·14165 | 0·30103 | 0·4705 | 0·6982 |
| 0·002 | 0·9709 | 1·53611 | 4·44270 | 0·13755 | 0·30104 | 0·4569 | 0·6852 |
| 0·005 | 0·9562 | 1·35853 | 4·04474 | 0·17758 | 0·39796 | 0·4462 | 0·6638 |
| 0·01 | 0·9410 | 1·22915 | 3·74367 | 0·12938 | 0·30107 | 0·4297 | 0·6427 |
| 0·02 | 0·9218 | 1·10679 | 3·44248 | 0·12236 | 0·30119 | 0·4062 | — |
| 0·05 | 0·8891 | 0·95507 | 3·04419 | — | — | — | — |
| 0·1 | 0·8600 | 0·85387 | 2·74257 | — | — | — | — |
| 0 2 | 0·8276 | 0·76346 | 2·44037 | — | — | — | — |

FIG. 3.



are set out in Fig. 3. We get as before a straight line with the coefficient 0·5 for $x$, and the limiting value of the constant the same as before.

Other strong electrolytes of the same class, such, for instance, as sodium chloride and lithium chloride, yield the same exact coefficient 0·5 at infinite dilution, although, of course, the constant differs in each case.

We now see that we can get any number of formulæ of the same form which are equally true in the limit. We may set out the three which have been above investigated, together with two others of the same form which are of some interest:

$$\text{Rudolphi:} \quad \frac{\alpha^2}{1-x} = \frac{h^{\frac{1}{2}}}{5{\cdot}37}$$

$$\text{Van't Hoff:} \quad \frac{\alpha^{\frac{3}{2}}}{1-\alpha} = \frac{h^{\frac{1}{2}}}{5{\cdot}37}$$

$$\text{Limiting relation:} \quad \frac{1}{1-\alpha} = \frac{h}{5{\cdot}37}$$

$$\text{New relation:} \quad \frac{\alpha}{1-\alpha} = \frac{h^{\frac{1}{2}}}{5{\cdot}37}$$

$$\text{Kohlrausch:} \quad \frac{\alpha^n}{1-\alpha} = \frac{h^{\frac{1}{2}}}{5{\cdot}37}.$$

It will be seen that in the region of very high dilution we can have the index of $\alpha$ anything we please within wide limits. If we make it simply unity we get the new relation which is the fourth above. This particular formula is of interest because we can make it an exact relation down to decinormal dilution by multiplying by the simple exponential factor $10^{1-\alpha}$, which gives the equation:

$$\frac{\alpha}{1-\alpha} = h^{\frac{1}{2}} \frac{10^{1-\alpha}}{5{\cdot}37}.$$

This is an equation which may possibly have a theoretical meaning, and is of practical utility, as it will serve, equally with the Kohlrausch equation, for extrapolation to the value of $\lambda_\infty$.

Having so much flexibility in the index of $\alpha$, we may choose for the index a value which will make the value of $\alpha$ come out accurate at any given dilution—say, twice decinormal. The required value of the index of $\alpha$ is:

$$n = 3{\cdot}311.$$

This is the equation used by Kohlrausch for extrapolating to get $\lambda_\infty$. The value of $n$ is slightly different from his value, since we are taking $\alpha = \lambda\eta/\lambda_\infty$.

In table IV are set out the values of $\alpha$ obtained from Kohlrausch, from the exponential formula, from Rudolphi, and from van't Hoff. The equations are solved for $\alpha$ by making a table of values of $\alpha$ for each equation. It will be seen that the Kohlrausch formula gives values which are practically the exact values of $\alpha=\lambda\eta/\lambda_\infty$, the new exponential formula gives these exact values

### TABLE IV.

*Values of* $\alpha$.

| $m$. | $\alpha=\lambda\eta/\lambda_\infty$. | Kohl-rausch. | Diff. | New exponential formula. | Diff. | Rudolphi. | Diff. | van't Hoff. | Diff. |
|---|---|---|---|---|---|---|---|---|---|
| 0·0001 | 0·992 | 0·992 | ± | 0·992 | ± | 0·992 | ± | 0·992 | ± |
| 0·0002 | 0·990 | 0·990 | ± | 0·990 | ± | 0·990 | ± | 0·990 | ± |
| 0·0005 | 0·985 | 0·985 | ± | 0·985 | ± | 0·984 | −1 | 0·984 | −1 |
| 0·001 | 0·979 | 0·979 | ± | 0·979 | ± | 0·978 | −1 | 0·978 | −1 |
| 0·002 | 0·971 | 0·971 | ± | 0·971 | ± | 0·970 | −1 | 0·969 | −2 |
| 0·005 | 0·956 | 0·956 | ± | 0·956 | ± | 0·954 | −2 | 0·952 | −4 |
| 0·01 | 0·941 | 0·941 | ± | 0·941 | ± | 9·936 | −5 | 0·934 | −7 |
| 0·02 | 0·922 | 0·922 | ± | 0·922 | ± | 0·914 | −8 | 0·910 | −12 |
| 0·05 | 0·889 | 0·890 | +1 | 0·889 | ± | 0·876 | −13 | 0·868 | −21 |
| 0·1 | 0·860 | 0·861 | +1 | 0·859 | −1 | 0·839 | −21 | 0·826 | −34 |
| 0·2 | 0·828 | 0·828 | ± | 0·823 | −5 | 0·795 | −33 | 0·776 | −52 |

down to decinormal solutions, the Rudolphi and van't Hoff formulæ gives values which are within one part in a thousand down to a dilution of $N/1000$ only.

Between these formulæ how is one to determine which gives most nearly the true values of $\alpha$? One thing is quite clear. The two formulæ which give the exact values for $\alpha=\lambda\eta/\lambda_\infty$ cannot be the right formulæ for the true value of $\alpha$, since they leave no margin for the change of $\alpha$ due to the change of mobility which is brought about by variations of ionic size. Empirical correspondences over a long range do not help us, and the only test is to be found by a consideration of other physical properties which depend on $\alpha$.

In a former paper (Bousfield, *Phil. Trans.*, 1906, *A*, **206**, 101) the matter was approached on the following lines. Starting with the van't Hoff law, which was shown to be true in the limiting case of infinite dilution, and taking the series of values of $\alpha=\lambda\eta/\lambda_\infty$ which correspond accurately with the van't Hoff law in the highest ranges of dilution, it was assumed that the departures of these values of $\alpha$ from those given by the van't Hoff law in the lower ranges of dilution were due to the fact that $\alpha$ was uncorrected for variations of ionic size. It was thus possible, on this assumption, to work out the variations of ionic size which would bring the van't Hoff law into accord with the experimental values of $\alpha$ at such lower dilutions. On this assumption the varying ionic radius was found to be represented by:

$$r=l^{-1}(1+Bh^{-\frac{2}{3}})^{-1},$$

where $l$ is the mobility of the ion at infinite dilution. This enabled the varying volume of the ion to be traced, and hence the varying amount of water combination. It was found that the values of $\alpha$ and of the ionic sizes and of the amounts of combined water thus calculated were concordant with measurements of other physical properties into which these same elements entered. For this purpose the best of these properties is freezing-point depression, since the variation of freezing-point depression values with dilution is correlated to the amount of combined water, so that in this way we get back to change of ionic size, and so to change of mobility due to this cause. Working on these lines, it is shown in the former paper that the variations of ionic size, calculated on the hypothesis that the van't Hoff formula is the right one, do, in fact, lead to values for the combined water which in conjunction with the values of $\alpha$ yielded by the formula are in good accord with experimental determinations of the variations of the freezing-point values with dilution. It will be seen from table IV that the values of $\alpha$ yielded by the Rudolphi formula are practically the same as those given by the van't Hoff formula in the higher ranges of dilution, and only differ from them by two parts in a thousand at a dilution of $N/100$. It follows that the values for the ionic sizes yielded by the Rudolphi formula will not differ greatly in this range from those given by the van't Hoff formula. It remains, however, to examine the values for the ionic sizes which Rudolphi's formula would yield at lower dilutions to see if they are in better or worse agreement with freezing-point depression values and other physical properties—a somewhat delicate and tedious investigation which must stand over for the present. In the meantime as either of these formulæ is in good accord with the variations of freezing-point depressions over a considerable range of dilution, it seems better for various practical purposes to use the values of $\alpha$ derived from one of these two formulæ, rather than to take values of $\alpha$ which are obtained in a more conjectural manner. The matter has been illustrated only by reference to potassium chloride, but these formulæ apply equally, with a change of the constant, to sodium chloride, lithium chloride, and a number of other strong electrolytes.

The difficulty of choice between the formulæ does not, however, meet us in the region of highest dilution. Here all the formulæ which we have examined become the same, and we may say with confidence that in this region there is no doubt about the true relation between ionisation and dilution in this class of "strong" electrolytes. They all reduce to the simple dilution law

$$(1-\alpha)=h^{-\frac{1}{3}}\times\text{Constant}.$$

In the same region the Ostwald law for "weak" electrolytes reduces to

$$(1-\alpha)=h^{-1}\times \text{Constant.}$$

Here the mass relation appears in its simplest terms, since in both cases progressive hydration has proceeded so far that molecular varieties have been reduced to the fewest. These two simple formulæ thus bring out the fundamental difference between the class of "weak" electrolytes of which acetic acid is an example, and the class of "strong" electrolytes, of which potassium chloride is an example.

*For weak electrolytes the active mass of the undissociated fraction at great dilution is inversely proportional to the mass of the water.*

*For strong electrolytes the active mass of the undissociated fraction at great dilution is inversely proportional to the square root of the mass of the water.*

Here, where the problem is simplest, is the point where reconciliation with the law of mass action as usually enunciated must begin. It is proposed to consider this aspect of the matter in a subsequent paper.

St. Swithins,
Hendon, N.W.

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## XXXIX.—*Viscosity and Association. Part IV. The Viscosity of the Aromatic Amines.*

By **Ferdinand Bernard Thole.**

The mutual effect of different unsaturated nuclei in a molecule has been studied from many points of view and by many different methods, both chemical (compare V. Meyer, Sudborough, and their co-workers, and Clarke) and physical. The main drawback attached to the former method lies in the undoubtedly very complex and sensitive nature of the inter-atomic forces which are greatly influenced, even by the addition of a comparatively inert solvent, and necessarily to a much greater degree by chemically active reagents.

Some time ago (T., 1910, **97**, 2596) the author investigated by the viscometric method the influence of various substituents in various spatial positions on the degree of association of phenol.

The results agreed closely with those derived from other physical properties, and showed that ortho-substitution has the greatest, and para-substitution the least, influence on the associating tendency of the hydroxyl group.

More important, however, is the nature of the substituent groups. Those which exhibit a considerable degree of unsaturation have the greatest effect in repressing association presumably by "binding" some of the residual affinity of the hydroxyl group. It was found possible, in fact, to arrange in series a number of common radicles in order of their inhibiting influence on phenolic association, and this order exactly paralleled with that obtained by arranging the same groups in order of their influence on molecular magnetic rotation. The most active of these were the carbethoxyl, aldehyde, and nitro-radicles, and the least active the chlorine and methyl radicles.

Investigation of solutions of the phenols in various solvents, both "dissociating" and "non-dissociating," showed the great extent of aggregate-disruption that was produced even by solvents of the latter class.

In the present paper a number of aromatic amines have been investigated with a view to ascertain whether the amino-group (which, like the hydroxyl group, possesses considerable residual affinity) is affected in the same way by substituent groups of varying residual affinity in varying positions in the benzene nucleus. This work also appeared of considerable interest, since a recent investigation on the viscosity of the amines (Mussell, Thole, and Dunstan, T., 1912, **101**, 1008), although carried out from a somewhat different point of view, directed attention to certain molecular influences which exert a very notable effect on viscosity. By comparing the values of $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ it was shown that as a general rule secondary amines are less viscous than primary amines, whilst tertiary amines are still less viscous, that is, the substitution of amino-hydrogen atoms by alkyl groups depresses viscosity, owing either to some specific property of the hydrogen atom or to the increasing symmetry of the molecule. When, however, these hydrogen atoms are replaced by groups containing centres of unsaturation, such as the acetyl, phenyl, benzyl, and to a less degree the allyl residues, the viscosity of the amine is enhanced instead of being diminished. This new influence, which overwhelms or at least profoundly modifies the other factors involved, was termed "reinforced conjugation."

Certain anomalies which have been observed in other series of compounds, both aromatic and aliphatic, have also been shown to be due to the existence of this molecular condition (Dunstan, Hilditch, and Thole, this vol., p. 133).

## EXPERIMENTAL.

The apparatus used in this work was of the new pattern recently described by the author (this vol., p. 22), and the experimental methods were similar to those detailed in previous communications.

The materials used were partly purchased and partly prepared by well known methods. In each case they were carefully purified before use.

Whenever possible the amines were investigated in the fused condition, but as many are solid at temperatures below 100° it proved necessary to compare their viscosities in some comparatively neutral solvent. The liquid chosen was amyl acetate, which has proved a valuable solvent in previous work in this connexion in view of its comparatively small dissociating tendencies and its excellent solvent powers. It will, however, be noticed that even amyl acetate produces a considerable effect on the molecular condition of the solute.

The solutions used were of equimolecular strength, and were prepared by weighing 0·005 gram-molecule of the amine in a stoppered weighing bottle, and dissolving in 7 c.c. of amyl acetate a concentration usually equivalent to about 12 per cent. In a few cases where such concentrated solutions could not be prepared, a solution of one-half this concentration was investigated, and the equivalent values for the stronger solution obtained by extrapolation.

The viscosities of the fused amines were determined at 55° and those of the solutions at 25°, the temperatures of the thermostats being controlled between very narrow limits ($\pm 0{\cdot}05°$ and $\pm 0{\cdot}01°$ respectively) by sensitive toluene regulators.

The viscosity values for the pure amines have been compared by use of the expression $\frac{\eta}{\text{Mol. vol.}} \times 10^6$. The use of this quantity for comparison purposes is undoubtedly open to several objections, but previous work has shown that it offers the most suitable method at present available for comparing the viscosities of liquids, particularly where these are of similar chemical nature.

The results for the solutions have been compared by calculating the increase produced in the product viscosity × density × $10^6$ of the pure solvent per unit of molecular weight of the dissolved amine. This quantity is termed $\Delta$ in the table of results.

### TABLE I.—*Pure Amines at* 55°.

| Amine. | Density 55°/4° | Viscosity. | $\frac{\eta}{\text{Mol. vol.}} \times 10^6$. |
|---|---|---|---|
| Aniline | 0·9913 | 0·01709 | 182 |
| *o*-Chloroaniline | 1·182 | 0·01647 | 153 |
| *m*-Chloroaniline | 1·184 | 0·01764 | 164 |
| *p*-Chloroaniline | 1·178 | 0·01964 | 182 |
| *o*-Toluidine | 0·9700 | 0·01711 | 155 |
| *m*-Toluidine | 0·9603 | 0·01513 | 136 |
| *p*-Toluidine | 0·9593 | 0·01557 | 140 |
| *o*-Anisidine | 1·064 | 0·02211 | 191 |
| *p*-Anisidine | 1·092 | 0·03215 | 286 |
| Ethyl anthranilate | 1·088 | 0·03258 | 215 |
| Methylaniline | 0·9571 | 0·01084 | 96·9 |
| Ethylaniline | 0·9319 | 0·01081 | 83·3 |
| *iso*Amylaniline | 0·8912 | 0·01724 | 94·3 |
| Allylaniline | 0·9536 | 0·01414 | 101 |
| Diphenylamine | 0·9633 | 0·04660 | 266 |
| Benzylaniline | 1·038 | 0·05388 | 306 |
| Benzylideneaniline | 1·038 | 0·03985 | 229 |
| Methyl-*o*-toluidine | 0·9500 | 0·01171 | 92·0 |
| Methyl-*p*-toluidine | 0·9348 | 0·01220 | 94·2 |
| Ethyl-*o*-toluidine | 0·9220 | 0·01100 | 75·1 |
| Ethyl-*p*-toluidine | 0·9148 | 0·01211 | 82·1 |
| Dimethylaniline | 0·9274 | 0·00844 | 64·7 |
| Methylethylaniline | 0·9193 | 0·00972 | 66·2 |
| Diethylaniline | 0·9196 | 0·01102 | 68·0 |
| Di*iso*amylaniline | 0·8668 | 0·02923 | 109 |
| Methylallylaniline | 0·9242 | 0·01068 | 67·1 |
| Benzylethylaniline | 1·001 | 0·04772 | 226 |
| Dimethyl-*o*-toluidine | 0·9003 | 0·00881 | 58·7 |
| Dimethyl-*p*-toluidine | 0·9116 | 0·00864 | 58·3 |
| Dimethyl-α-naphthylamine | 1·013 | 0·03248 | 192 |
| Dimethyl-β-naphthylamine | 1·029 | 0·03365 | 202 |

### TABLE II.—*Solutions at* 25°.

| Amine. | Density 25°/4°. | Viscosity. | Δ. |
|---|---|---|---|
| Aniline | 0·8778 | 0·008845 | 9·0 |
| *o*-Chloroaniline | 0·8940 | 0·009250 | 10·5 |
| *m*-Chloroaniline | 0·8945 | 0·009521 | 12·5 |
| *p*-Chloroaniline | 0·8949 | 0·009591 | 13·0 |
| 2 : 4-Dichloroaniline | 0·9088 | 0·009788 | 12·9 |
| 2 : 4 : 6-Trichloroaniline | 0·9229 | 0·009851 | 11·0 |
| *o*-Bromoaniline | 0·9161 | 0·009663 | 11·5 |
| *p*-Bromoaniline | 0·9199 | 0·009845 | 12·7 |
| 2 : 4-Dibromoaniline | 0·9603 | 0·01041 | 12·2 |
| 2 : 6-Dibromoaniline | 0·9760 | 0·00997 | 11·2 |
| 2 : 4 : 6-Tribromoaniline | 1·002 | 0·01017 | 9·9 |
| *p*-Iodoaniline | 0·9530 | 0·01011 | 12·4 |
| 2 : 4-Di-iodoaniline | 1·021 | 0·01120 | 13·1 |
| *o*-Anisidine | 0·8842 | 0·009215 | 10·0 |
| *o*-Toluidine | 0·8771 | 0·008841 | 7·7 |
| *m*-Toluidine | 0·8763 | 0·008816 | 7·4 |
| *p*-Toluidine | 0·8763 | 0·008816 | 7·4 |
| Ethyl anthranilate | 0·8916 | 0·00992 | 11·6 |
| Ethyl *p*-aminobenzoate | 0·8943 | 0·01130 | 19·2 |
| *o*-Phenylenediamine | 0·8842 | 0·009834 | 16·3 |
| *m*-Phenylenediamine | 0·8868 | 0·01009 | 18·7 |
| *o*-Nitroaniline | 0·9015 | 0·01012 | 15·9 |
| *m*-Nitroaniline | 0·9011 | 0·01041 | 17·8 |
| α-Naphthylamine | 0·8893 | 0·01031 | 15·7 |
| β-Naphthylamine | 0·8898 | 0·01030 | 15·6 |
| Diphenylamine | 0·8944 | 0·01071 | 22·4 |

### *Discussion of Results.*

*Table I.*—The values obtained for the liquid amines bear out the results obtained in the previous communication on these substances. Moreover, the greater number and range of amines investigated afford new evidence as to the influence on the molecule of substitution in the amino-group and in the benzene nucleus.

Dealing first with the former type of substitution it is seen that as a general rule primary amines have a high viscosity, the secondary amines being less viscous and the tertiary still less so. In the two latter classes it will be noticed that the viscosity factor increases slowly with increasing molecular weight of the alkyl groups, although it still remains much smaller than the average value for a primary amine. The first member of the series, methylaniline, appears to be slightly anomalous, the viscosity being distinctly higher than that of ethylaniline.

When the amino-hydrogen atoms are replaced by groups possessing considerable residual affinity the above general rule is reversed, and the difference is most marked when the substituent group contains a phenyl nucleus; thus benzylaniline, diphenylamine, and benzylideneaniline are much more viscous even than aniline, whilst the viscosity of allylaniline, although of the same order of magnitude as the simple secondary amines, shows a quite evident exaltation due to the unsaturated character of the allyl grouping. In the case of the tertiary amines the powerful influence of the benzyl nucleus (for example, in benzylethylaniline) is still apparent, but in methylallylaniline the allyl group exerts but little exalting effect.

Since it is well known that increase in symmetry tends to diminish viscosity, it is evident that the exaltation produced by the introduction into the amino-group of unsaturated residues is due to what may be termed conjugated residual affinity. Its effect is shown much more markedly in this series of compounds than in any others hitherto examined, probably because three notably unsaturated nuclei are concerned.

Many other instances of this phenomenon may be cited, for example, the high viscosity of acetanilide as compared with that of aniline.

Owing to the inconveniently high melting points of many aniline derivatives, the influence of ortho-meta-para-substitution has not been studied very fully with the pure fused amines. It will be noticed, however, that as a general rule the ortho-compound has the lowest and the para the highest viscosity of the three isomerides, a condition which is in exact agreement with that found in the case of the phenols. The nature of the substituent group also has an important effect, alkyl and chlorine substituents depressing the viscosity of the parent amine, whilst carbethoxyl and methoxyl augment it.

*Table II.*—The very great alteration produced in the condition of the molecules of a solute by the addition of a solvent is most strikingly shown by the results obtained with the amyl acetate solutions. It will be noticed that the order of viscosities is in general considerably different from that followed by the pure amines, and only the more strongly marked characteristics of the latter persist in solution.

Moreover, the relative effects of conjugation in the benzene nucleus by *o*-, *m*-, and *p*-substituents, conjugation in the amino-nucleus, and symmetry are profoundly modified, the effect of the first being emphasised and of the last minimised by solution.

Considering the results in fuller detail it will be noticed that the least viscosity increment is produced by the toluidines. The depressing effect of the substituent methyl group has already been pointed out in connexion with the results in table I.

A further striking point is the comparatively great reduction produced in the viscosity of aniline and the toluidines by solution.

The progressive substitution of the benzene ring by halogens produces particularly interesting results. Considering first the chlorine derivatives, it will be observed that the viscosity of aniline is augmented by chlorination, the ortho-substituent having the least and the para the greatest effect. Further substitution, however, depresses the viscosity increment slightly in 2:4-dichloroaniline and to a considerably greater degree in trichloroaniline.

In the bromo-derivatives a similar but more marked effect is evident, tribromoaniline having a particularly low viscosity. Moreover, the viscosity of 2:6-dibromoaniline is considerably less than that of the 2:4-isomeride, where the bromine atoms are less intimately associated with the amino-group.

*p*-Iodoaniline has a still lower viscosity than the chloro- or bromo-compounds, but in 2:4-di-iodoaniline the viscosity rises again, probably owing to the highly unsymmetrical loading of the benzene ring.

Whereas the alkyl and methoxyl groups and the halogen atoms have a depressing or very slightly elevating action on the viscosity of the parent amine substitution of the carbethoxyl, nitro- and amino-complexes in the benzene nucleus has a most marked effect in raising the viscosity, the value of the increment rising to about 19. With the phenylenediamines and nitroanilines this figure is almost reached by the meta-compounds, and from analogy to the other series examined the para-compound would give a value even in excess of this. Unfortunately, experimental verification was prevented by the sparing solubility of the substances in question.

The same effect, although to a more modified degree, is shown in the naphthylamines, where a fused benzene ring takes the place of a simple substituent.

It is noteworthy that the nitro- and carbethoxyl groups which enhance so considerably the viscosity increment in this series are also the most active in repressing the association of phenol, and, further, together with the amino-group, produce very marked anomalies in the molecular refractivity of their benzenoid derivatives.

A still further point of interest lies in the fact that the difference between the viscosity of ortho- and para-isomerides is greatest in the case of the aminobenzoic esters and nitroanilines, and least with the alkyl and halogen derivatives.

Apart from these few parallels, however, there is little resemblance between the behaviour of phenols and amines when substituted by different groups. In the former compounds apparently the only variable condition which affects the viscosity to any notable extent is the degree of association, and this is almost exclusively connected with the position and degree of residual affinity of the substituting group. Moreover, the action of the solvent was merely to decrease greatly the association without producing any alteration in the order of the degree of influence of the groups.

In the amines, on the other hand, one has the effect of the conflicting variables of association, conjugation in the amino-group and in various positions in the benzene nucleus, and symmetry brought out in a very marked manner. Moreover, these influences are considerably affected and to very different extents by the influence of the solvent.

So complex, in fact, is the net result of the various factors which influence the viscosity of these compounds that it is desirable at present not to do more than direct attention to the general regularities that are apparent, without pressing too far speculations on the resultant effect of such a complex system of intramolecular and intermolecular forces.

The author desires to express his indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly covered the expenses of the research.

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# XL.—*The Reaction between Ferric Salts and Thiosulphates.*

By JOHN THEODORE HEWITT and GLADYS RUBY MANN.

AMONGST the comparatively few quadrimolecular reactions which have been studied, reference may be made to the reduction of chromic acid by phosphorous acid (G. Viard, *Compt. rend.*, 1897, **124**, 148), the interaction of hydrobromic and bromic acids (W. Judson and J. W. Walker, T., 1898, **73**, 410), the bromination of benzene (L. Bruner, *Zeitsch. physikal. Chem.*, 1902, **41**, 513), and the decomposition of potassium chlorate at 395° (J. Scobai, *Zeitsch. physikal. Chem.*, 1903, **44**, 319). Of these reactions the first and second appear to be fairly straightforward, although it should be noted that the decomposition of hydrochloric and chloric acids appears to be of the eighth order, which is to be explained on the assumption that the reaction depends on the ions of the respective acids (R. Luther and F. H. MacDougall, *Zeitsch. physikal Chem.*, 1908, **62**, 199):

$$4H^{\cdot} + 2Cl' + 2ClO_3' = 2ClO_2 + Cl_2 + 2H_2O.$$

The bromination of benzene and the decomposition of potassium chlorate are attended by side-reactions, so that an addition to the known number of quadrimolecular reactions appears desirable.

Our attention was called to the reaction between ferric salts and sodium thiosulphate in working out a method for estimating the relative amounts of ferrous and ferric iron present in a solution containing considerable quantities of organic matter (*Analyst*, 1912, **37**, 179). The presence of organic matter precluded the use of permanganate or dichromate for oxidation of the ferrous iron; reduction of the ferric iron with stannous or titanous chlorides was equally undesirable on account of the well-known behaviour of these reagents towards easily reducible organic substances. The use of sodium thiosulphate as a reducing agent for the ferric salts offered a possible solution of the difficulty, and eventually satisfactory results were obtained in so far as the estimation of the iron in the two states of oxidation was concerned. At the same time our attention was drawn to the slowness of the reaction between certain ferric compounds and thiosulphates, so that we considered it advisable to measure the rate of reaction and determine the velocity constants in certain cases.

A ferric salt on reduction with a thiosulphate ought to behave as if the reaction were of the fourth order in accordance with the equation:

$$2Fe^{\cdot\cdot\cdot} + 2S_2O_3'' = 2Fe^{\cdot\cdot} + S_4O_6'',$$

although the possibility of an apparently bimolecular reaction is not excluded if the reaction takes place in two successive stages:

$$Fe^{\cdot\cdot\cdot} + S_2O_3'' = Fe^{\cdot\cdot} + S_2O_3'$$
$$2S_2O_3' = S_4O_6'',$$

the second stage being more rapid than the first.

Anomalies are occasionally found in reduction by thiosulphates; thus the reaction between hydrogen peroxide and thiosulphates in acid solution:

$$H_2O_2 + 2S_2O_3'' + 2H^{\cdot} = S_4O_6'' + 2H_2O,$$

is apparently bimolecular; as an explanation the separation of electrically neutral $S_2O_3$ has been given (Emil Abel, *Monatsh.*, 1907, **28**, 1239).

Whilst the reduction of salts like ferric chloride is too rapid for determination of the velocity of the reaction, ferric alum and solutions containing thiocyanates, phenol, etc., were found to be measurable; the reactions were always of the fourth order, and consequently one may conclude that it is necessary that four molecules or ions react simultaneously and the transient existence of ions, $S_2O_3'$, is excluded. The constancy of the "constants" determined leaves much to be desired, but when it is borne in mind that the reaction between $N/80$-solutions of iron (as ferric alum) and sodium thiosulphate is half completed in about eleven minutes at 0°, it will be seen that the experimental work is not of the easiest; whilst the choice of 0° instead of 25° for carrying out the reaction, and the abandonment of attempts to measure the velocities of the reactions between sodium thiosulphate and ferric chloride or of ferric solutions to which only 3 molecules of potassium thiocyanate had been added per atom of iron, will occasion no surprise. The velocities actually determined were those of the reactions between $N/80$-sodium thiosulphate and $N/80$-ferric alum alone or with addition of 4 or 12 molecules of potassium thiocyanate, 4 molecules of phenol, or 4 molecules of ethyl acetoacetate. In all these cases there was no doubt that the reaction was of the fourth order; calculation showed that any other order of reaction was excluded.

## EXPERIMENTAL.

Stock solutions were made of ammonia iron alum and sodium thiosulphate. The former contained 2·7925 grams of iron per litre, and was made by weighing out an exact amount of the alum in which the iron had been gravimetrically estimated. (Found, 11·65 and 11·62. Theory, 11·58.) The sodium thiosulphate was $N/40$ (6·2055 grams per litre). In carrying out a measurement, all solutions were cooled to 0°, 25 c.c. of the iron solution were transferred to a flask previously cooled, 25 c.c. of water or of a solution of thiocyanate, phenol, etc., added; then 50 c.c. of the thiosulphate solution, and the time noted. Samples of 10 c.c. were withdrawn at intervals of about 2 minutes, and transferred to flasks containing excess of solution of disodium phosphate and sodium acetate; both ferrous and ferric salts were thus precipitated, and further reaction of the ferric salt with the thiosulphate prevented. After addition of starch the remaining thiosulphate was titrated with $N/80$-iodine; the number of c.c. used, subtracted from 10, gave the number of c.c. of thiosulphate which had already reacted with the ferric solution. No inconvenience was caused by the presence of the phosphates of iron. The units employed in calculating the reaction constants from the formula for a quadrimolecular reaction:

$$k=\frac{1}{t}\cdot\frac{1}{3}\left\{\frac{1}{(a-x)^3}-\frac{1}{a^3}\right\}$$

are arbitrary. $a=10$ (that is, the number of c.c. of reacting mixture withdrawn for each titration); $a-x$ is then given directly by the number of c.c. of iodine used in titrating the unused thiosulphate. The constants recorded must be multiplied by $80^3$ if the results are desired for normal solutions (1 c.c. being still the unit of volume).

### (i) *Ferric Alum and Thiosulphate.*

25 C.c. $N/20$-ferric alum solution, 25 c.c. distilled water, 50 c.c. $N/40$-sodium thiosulphate.

$$t=\text{seconds},\ a=10,\ k=\frac{1}{t}\cdot\frac{1}{3}\left\{\frac{1}{(a-x)^3}-\frac{1}{a^3}\right\}.$$

I.

| $t$. | $a-x$. | $k$. |
|---|---|---|
| 133 | 7·69 | $0·3007 \times 10^{-5}$ |
| 279 | 6·50 | 0·3156 |
| 402 | 5·82 | 0·3375 |
| 529 | 5·58 | 0·2997 |
| 646 | 5·02 | 0·3563 |
| 804 | 4·69 | 0·3603 |
| 954 | 4·39 | 0·2385 |
| 1078 | 4·14 | 0·4047 |
| 1257 | 3 95 | 0·4039 |
| | Mean......... | $0·3365 \times 10^{-5}$ |

II.

| $t$. | $a-x$. | $k$. |
|---|---|---|
| 113 | 7·95 | $0·2920 \times 10^{-5}$ |
| 248 | 5·78 | 0·2970 |
| 374 | 5·93 | 0·3382 |
| 516 | 5·40 | 0·3457 |
| 663 | 5·00 | 0·3511 |
| 819 | 4·69 | 0·3539 |
| 1017 | 4·23 | 0·4005 |
| 1128 | 4·18 | 0·3646 |
| | Mean......... | $0·3419 \times 10^{-5}$ |

Mean of both series, $0·3392 \times 10^{-5}$.

### (ii) *Ferric Alum, Potassium Thiocyanate, and Thiosulphate.*

In the first experiments made on the rate of reaction of solutions of ferric thiocyanate (iron alum and potassium thiocyanate), an attempt was made to follow the course of the reaction colorimetrically. Although the results obtained furnished no useful constants, it was found that whilst the reaction proceeded rapidly when only three molecular proportions of potassium thiocyanate were added per atom of ferric iron, the rate of reduction by sodium thiocyanate was greatly reduced when the potassium thiocyanate was added in considerable excess to the ferric solution. The results obtained with 4 and 12 molecules of potassium thiocyanate per atom of iron are recorded.

### (ii*a*) $1Fe : 4KCNS : 1Na_2S_2O_3$.

25 C.c. *N*/20-ferric alum, 25 c.c. 4*N*/20-KCNS,
50 c.c. *N*/40-sodium thiosulphate.

| *t.* | *a − x.* | *k.* | *t.* | *a − x.* | *k.* | *t.* | *a − x.* | *k.* |
|---|---|---|---|---|---|---|---|---|
| 129 | 4·66 | $2·295 \times 10^{-5}$ | 129 | 4·55 | $2·485 \times 10^{-5}$ | 144 | 4·45 | $2·395 \times 10^{-5}$ |
| 249 | 3·65 | 2·620 | 265 | 3·60 | 2·571 | 289 | 3·45 | 2·693 |
| 374 | 3·05 | 3·055 | 402 | 3·09 | 2·727 | 483 | 2·91 | 2·731 |
| 504 | 2·86 | 2·232 | 534 | 2·81 | 2·812 | 659 | 2·67 | 2·608 |
| 613 | 2·67 | 2·802 | 649 | 2·60 | 2·871 | 858 | 2·46 | 2·572 |
| 760 | 2·43 | 3·012 | 783 | 2·49 | 2·715 | 1008 | 2·26 | 2·839 |
| 907 | 2·31 | 2·945 | 929 | 2·32 | 2·837 | 1174 | 2·19 | 2·673 |
| 1095 | 2·19 | 2·868 | 1098 | 2·19 | 2·860 | 1388 | 1·99 | 3·021 |
| 1220 | 2·19 | 2·574 | 1224 | 2·11 | 2·938 | 1550 | 1·93 | 2·969 |
| Mean... | | $2·712 \times 10^{-5}$ | Mean... | | $2·757 \times 10^{-5}$ | Mean .. | | $2·722 \times 10^{-5}$ |

**Mean of three series, $2·730 \times 10^{-5}$.**

It will be seen that the reaction is half completed in about two minutes, and great constancy of *k* is not to be expected.

### (ii*b*) $1Fe : 12KCNS : 1Na_2S_2O_3$.

25 C.c. *N*/20-ferric alum, 25 c.c. 12*N*/20-KCNS,
50 c.c. *N*/40-sodium thiosulphate.

| *t.* | *a − x.* | *k.* | *t.* | *a − x.* | *k.* |
|---|---|---|---|---|---|
| 109 | 7·40 | $0·4492 \times 10^{-5}$ | 268 | 6·05 | $0·4438 \times 10^{-5}$ |
| 262 | 6·09 | 0·4262 | 451 | 5·35 | 0·3993 |
| 394 | 5·50 | 0·3331 | 563 | 4·91 | 0·4211 |
| 494 | 5·22 | 0·4069 | 698 | 4·69 | 0·4151 |
| 613 | 4·91 | 0·4056 | 809 | 4·42 | 0·4343 |
| 783 | 4·64 | 0·3836 | 958 | 4·28 | 0·4092 |
| 1019 | 4·33 | 0·3707 | 1090 | 4·09 | 0·4165 |
| 1124 | 4·09 | 0·3622 | 1225 | 3·96 | 0·4110 |
| 1270 | 3·92 | 0·4096 | | | |
| Mean......... | | $0·3945 \times 10^{-5}$ | Mean......... | | $0·4188 \times 10^{-5}$ |

**Mean of both series, $0·4066 \times 10^{-5}$.**

### (iii) *Ferric Alum, Phenol, and Sodium Thiosulphate.*

25 C.c. *N*/20-ferric alum, 25 c.c. 4*N*/20-phenol solution, 50 c.c. *N*/40-sodium thiosulphate.

| *t.* | *a – x.* | *k.* | *t.* | *a – x.* | *k.* |
|---|---|---|---|---|---|
| 109 | 7·91 | 0·3120 $\times 10^{-5}$ | 253 | 6·69 | 0·3083 $\times 10^{-5}$ |
| 258 | 6·51 | 0·3390 | 398 | 5·79 | 0·3477 |
| 409 | 6·17 | 0·2656 | 609 | 5·09 | 0·3604 |
| 533 | 5·53 | 0·3074 | 779 | 4·71 | 0·3660 |
| 644 | 5·10 | 0·3384 | 933 | 4·40 | 0·3835 |
| 785 | 4·71 | 0·3631 | 1075 | 4·35 | 0·2815 |
| 929 | 4·47 | 0·3658 | 1349 | 3·86 | 0·4049 |
| 1060 | 4·30 | 0·3640 | 1414 | 3·88 | 0·3631 |
| 1163 | 4·06 | 0·4032 | | | |
| | Mean......... | 0·3398 $\times 10^{-5}$ | | Mean..... ... | 0·3519 $\times 10^{-5}$ |

| *t.* | *a – x.* | *k.* | *t.* | *a – x.* | *k.* |
|---|---|---|---|---|---|
| 194 | 7·19 | 0·2906 $\times 10^{-5}$ | 132 | 7·80 | 0·2796 $\times 10^{-5}$ |
| 332 | 6·21 | 0·3189 | 268 | 6·55 | 0·3184 |
| 493 | 5·68 | 0·2995 | 407 | 5·75 | 0·3488 |
| 614 | 5·12 | 0·3501 | 537 | 5·30 | 0·3548 |
| 738 | 5·09 | 0·2974 | 674 | 5·00 | 0·3461 |
| 909 | 4·48 | 0·3710 | 823 | 4·66 | 0·3602 |
| 1038 | 4·33 | 0·3634 | 982 | 4·46 | 0·3485 |
| 1227 | 3·96 | 0·4103 | 1108 | 4·28 | 0·3536 |
| 1359 | 3·85 | 0·4053 | 1252 | 4·03 | 0·3800 |
| | Mean ........ | 0·3452 $\times 10^{-5}$ | | Mean......... | 0·3322 $\times 10^{-5}$ |

Mean of four series, 0·3423 $\times 10^{-5}$.

### (iv) *Ferric Alum, Ethyl Acetoacetate, and Sodium Thiosulphate.*

25 C.c. *N*/20-ferric alum, 25 c.c. 4*N*/20-ethyl acetoacetate, and 50 c.c. *N*/40-sodium thiosulphate.

Considerable difficulty was at first experienced in titrating with *N*/80-iodine, probably on account of reaction of the halogen with the acetoacetate. Mr. A. D. Mitchell suggested that considerable dilution and addition of excess of potassium iodide might obviate the difficulty, and, using this suggestion, fair results were obtained.

| *t.* | *a – x.* | *k.* | *t.* | *a – x.* | *k.* | *t.* | *a – x.* | *k.* |
|---|---|---|---|---|---|---|---|---|
| 119 | 8·44 | 0·1860 $\times 10^{-5}$ | 164 | 7·31 | 0·3172 $\times 10^{-5}$ | 128 | 7·78 | 0·2925 $\times 10^{-5}$ |
| 303 | 6·45 | 0·3000 | 449 | 5·91 | 0·2886 | 302 | 6·40 | 0·3106 |
| 508 | 5·47 | 0·3353 | 593 | 5·24 | 0·3340 | 444 | 5·91 | 0·2886 |
| 1025 | 5·02 | 0·2694 | 738 | 4·99 | 0·2970 | 599 | 5·26 | 0·3279 |
| 1215 | 4·28 | 0·3226 | 1079 | 4·54 | 0·2990 | 952 | 4·75 | 0·2918 |
| 1408 | 4·08 | 0·3244 | 1255 | 4·01 | 0·3854 | 1322 | 4·09 | 0·3434 |
| 1644 | 4·01 | 0·2943 | 1395 | 3·79 | 0·4248 | 1457 | 4·02 | 0·3293 |
| | Mean .. | 0·2903 $\times 10^{-5}$ | | Mean... | 0·3381 $\times 10^{-5}$ | | Mean... | 0·3120 $\times 10^{-5}$ |

Mean of three series, 0·3135 $\times 10^{-5}$.

### (v) *Other Ferric Compounds.*

Originally it was intended to determine velocity constants for ferric solutions to which other substances than those mentioned above had been added. The homologues of phenol proved to be insufficiently soluble in water and ferric solutions to which four molecular proportions of sodium acetate had been added, whilst reacting slowly, proved quite useless owing to deposition of basic ferric acetate.

The results with acetylacetone were interesting. Solutions containing ferric alum and acetylacetone are very slowly decolorised by sodium thiosulphate; our expectation of measuring the velocity constant with ease was disappointed, for it was found that such solutions were not immediately precipitated by a mixture of sodium phosphate and acetate.

### *Conclusions.*

The comparatively slow reduction of ammonia ferric alum as compared with ferric chloride or solutions of ferric thiocyanate containing only a small excess of potassium thiocyanate, point to the iron being present as part of a complex negative ion in such solutions. These ions might arise by dissociation of the ammonium ferrisulphate in one of the two following ways:

$$(NH_4)_2Fe_2(SO_4)_4 \rightleftharpoons 2(NH_4)^{\cdot} + Fe_2(SO_4)_4{}''$$

or

$$(NH_4)Fe(SO_4)_2 \rightleftharpoons (NH_4)^{\cdot} + Fe(SO_4)_2{}'.$$

Since the reaction is quadrimolecular, two complexes containing iron must react with two thiosulphate ions; hence the second ionisation scheme for the ammonium ferrisulphate appears more probable.

NOTE.—A recent paper by Vorländer (*Ber.*, 1913, **46**, 181) deals with the production of Prussian blue from a ferric salt and ferrocyanide as a time-reaction. The time taken in the production of a precipitate is explained on the ground that ferric salts form incomplete colloidal solutions; whilst this explanation may hold in the case examined by Vorländer, the retardation of many ferric reactions can be explained by the formation of complex negative ions or of very slightly dissociated complexes.

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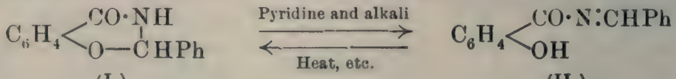
# XLI.—*Hexahydropyrimidine and its Benzoyl Derivatives.*

By Arthur Walsh Titherley and Gerald Eyre Kirkwood Branch.

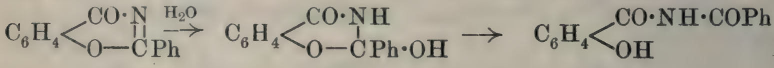
The object underlying the synthesis of hexahydropyrimidine and its benzoyl derivatives, described in the present paper, was to study the tautomeric relations which it was anticipated would obtain between the cyclic and open-chain forms. It has already been shown by one of the authors (T., 1907, **91**, 1423) that reduced oxazine-one derivatives of the type of 2-phenyldihydro-1:3-benzoxazine-4-one (I) may undergo reversible isomeric change to the open-chain isomeride, *syn*-benzylidenesalicylamide (II), thus:



$$C_6H_4<\begin{matrix}CO\cdot NH\\ O—CHPh\end{matrix} \underset{\text{Heat, etc.}}{\overset{\text{Pyridine and alkali}}{\rightleftarrows}} C_6H_4<\begin{matrix}CO\cdot N:CHPh\\ OH\end{matrix}$$

(I.) (II.)

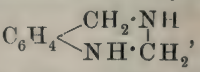
Further (T., 1910, **97**, 201), whilst the unsaturated 2-phenyl-1:3-benzoxazine-4-one (III) presents a stable ring *per se* (although easily ruptured by hydrolytic agents), addition of the elements of water gives the unstable saturated ring, 2-hydroxy-2-phenyldihydro-1:3-benzoxazine-4-one (IV), which immediately by rearrangement passes into the stable open-chain isomeride, *N*-benzoylsalicylamide (V):



$$C_6H_4<\begin{matrix}CO\cdot N\\ O—CPh\end{matrix} \xrightarrow{H_2O} C_6H_4<\begin{matrix}CO\cdot NH\\ O—CPh\cdot OH\end{matrix} \longrightarrow C_6H_4<\begin{matrix}CO\cdot NH\cdot COPh\\ OH\end{matrix}$$

(III.) (IV.) (V.)

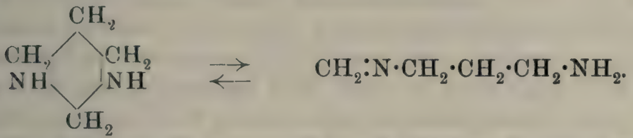
Similar examples of extremely unstable saturated oxazine-one rings which rearrange to the isomeric open-chain forms by wandering of a hydrogen atom have been described among the 2-amino-series by Titherley and Hughes (T., 1911, **99**, 1493). Similar relations of ring instability might therefore be anticipated among hexahydropyrimidines, in which, as in the reduced oxazines, a similar six-membered ring is present, the oxygen atom having been replaced by the imino-group. Pyrimidines and partly reduced pyrimidines are known to present stable ring systems, and tautomeric or isomeric change involving an open-chain form is generally excluded. With the exception of tetrahydroquinazoline,



$$C_6H_4<\begin{matrix}CH_2\cdot NH\\ NH\cdot CH_2\end{matrix},$$

described by Busch (*J. pr. Chem.*, 1895, [ii], **51**, 129) and Gabriel (*Ber.*, 1903, **36**, 811), and allied derivatives, no reduced pyrimidines containing the $NH\cdot CH_2\cdot NH$-group appear to have been obtained. The compound obtained by Busch and Gabriel, although not strictly a hexahydropyrimidine derivative, could conceivably rearrange to the open-chain isomeride, $C_6H_4{<}\begin{smallmatrix}CH_2\cdot N{:}CH_2\\ NH_2\end{smallmatrix}$, and it is possible that this formula appears in the monohydrochloride, $C_8H_{10}N_2,HCl$ (*loc. cit.*), which it yields. Further work will be carried out to throw light on this point.

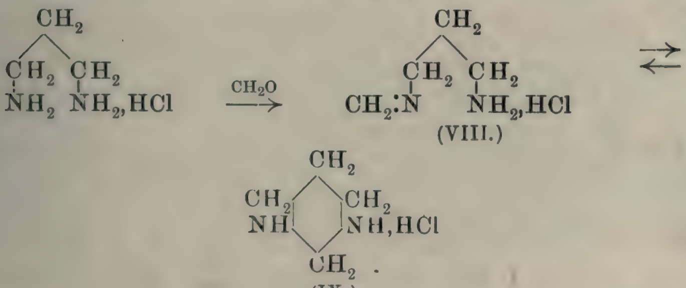
With the hitherto unknown simple hexahydropyrimidine (VI) it has been shown by the authors that tautomerism exists, involving make and break of the cyclic form, and producing the open-chain methylene-αγ-diaminopropane (VII), thus:



(VI.) Hexahydropyrimidine. (VII.) Methylene-αγ-diaminopropane.

Considerable difficulties were encountered in the synthesis of this tautomeric substance, which was obtained by the condensation of αγ-diaminopropane and formaldehyde, partly because of its easy hydrolysis by acids and partly because of the above reversible change. The condensation of αγ-diaminopropane and formaldehyde has already been studied by Bischoff and Reinfeld (*Ber.*, 1903, **36**, 35), who obtained ill-defined mixtures containing oxygen and apparently an impure dimethylene derivative, $CH_2{:}N[CH_2]_3\cdot N{:}CH_2$, owing to the fact that the reaction was not sufficiently controlled, condensation having occurred in several possible ways, as might be expected between such chemically reactive materials.

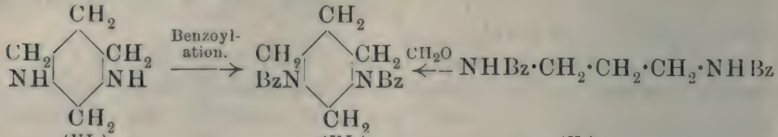
The authors have found, however, that by the action of aqueous formaldehyde on αγ-diaminopropane monoacetate or monohydrochloride simple condensation takes place, yielding an equilibrium mixture of salts (VIII and IX) of hexahydropyrimidine and its open-chain isomeride, in which the latter greatly predominates:



(VIII.)

(IX.)

This mixture on benzoylation in the presence of alkali functions exclusively as hexahydropyrimidine (VI), and gives an almost quantitative yield of 1:3-dibenzoylhexahydropyrimidine (XI), which has also been obtained in small yield by the condensation of formaldehyde and dibenzoyl-αγ-diaminopropane (X) in the presence of hydrochloric acid:



(VI.) (XI.) (X.)

When the above equilibrium mixture of salts is treated with alkali and extracted with ether a mixture of the two bases (VI and VII) is obtained, which on distillation yields a mobile, colourless liquid passing over at about 150°, leaving behind, with rising boiling point, a non-volatile, syrupy residue, which chars if attempts are made to distil it. The volatile fraction, however, rapidly undergoes isomeric change, and if redistilled it leaves behind a considerable fraction of the same syrupy substance, which is evidently methylene-αγ-diaminopropane. Moreover, it is slowly but completely changed into the same syrupy substance on keeping in contact with solid potassium hydroxide. It is clear from these facts that the tautomeric relation between the two bases is complicated by polymerisation. It is probable that the distillate boiling at 150° consists essentially of the cyclic base (VI) in equilibrium with small quantities of the open-chain isomeride (VII) and polymeric forms of the latter. On concentration (distillation) progressive polymerisation of the open-chain form takes place, in a similar manner to that of aqueous solutions of formaldehyde. The syrupy mixture of polymerides so obtained is readily soluble in water, with depolymerisation, yielding a strongly alkaline solution, evidently identical with the aqueous solution of the volatile distillate, since both on benzoylation yield the same 1:3-dibenzoylhexahydropyrimidine.

The behaviour of the mixture of bases in aqueous solution with hydrochloric acid is very striking. On titration to the neutral point with methyl-orange a value is obtained corresponding approximately with the monacidic open-chain base, but it is possible by gradual further addition of acid to obtain a value corresponding approximately with the diacidic cyclic base, and it would appear, therefore, that the stable form in the presence of two equivalents of acid is the salt of hexahydropyrimidine, the open-chain salt being present only to a very small extent.* This point, however, is uncertain owing to complication arising through hydrolysis. Although relatively stable in presence of alkali, the base (more probably the open-chain isomeride) is sensitive to hydrogen ions, and on long contact with acid more or less complete hydrolysis, with the formation of αγ-diaminopropane and formaldehyde, occurs. Unfortunately, no means were found of ascertaining the rate of hydrolysis, and therefore of fixing how far the second neutral point on titration with acid was determined by isomerisation and how far by the production of αγ-diaminopropane. It was found, however, that the apparent rate of isomerisation is lowered and not raised by excess of acid, and this is possibly due to inhibition of hydrolysis of the ammonium salt of the open-chain form in the partly reversible relation:

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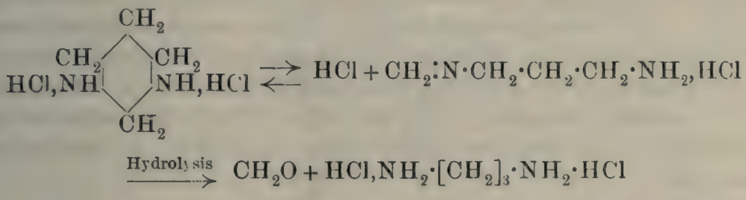
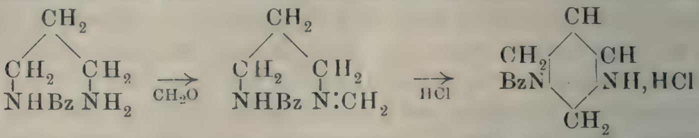
* These observations recall those of Titherley and Hughes (*loc. cit.*), in which it has been shown that 2-amino-2-phenyldihydrobenzoxazine-4-one derivatives are stable only as salts, and that in the free condition the open-chain isomerides only are stable.


CH2
CH2
CH2
HCl,NH
NH,HCl
CH2
HCl + CH2:N·CH2·CH2·CH2·NH2,HCl
Hydrolysis
CH2O + HCl,NH2·[CH2]3·NH2·HCl

Although this point has not been satisfactorily elucidated, evidence of the formation and existence of the cyclic dihydrochloride in the solution containing two equivalents of hydrochloric acid was obtained in the attempts to isolate the pure salt by evaporation in a vacuum, and by precipitating concentrated aqueous solutions with alcohol. In all cases the solid consisted of a mixture of the dihydrochlorides of hexahydropyrimidine and αγ-diaminopropane. Owing to partial hydrolysis it was found impossible to prepare any salt of hexahydropyrimidine in a pure condition.

In order to throw further light on hexahydropyrimidine tautomerism, attention was turned to the benzoyl derivatives. The dibenzoyl derivative already mentioned, in which both mobile hydrogen atoms are substituted, is, as would be expected, perfectly stable. Monobenzoylhexahydropyrimidine containing still a mobile hydrogen atom was next synthesised. It could not be obtained by incomplete benzoylation of the mixed bases, but was prepared by the condensation of formaldehyde and benzoyl-αγ-diaminopropane (XII), the synthesis of which from 2-phenyl-1:4:5:6-tetrahydropyrimidine by the authors has been described in a previous paper (T., 1912, **101**, 2348).

The product of the condensation is an amorphous, colourless solid with perfectly neutral properties, but on treatment with acid it rapidly combines with the latter to the extent of one equivalent. There can be no doubt, therefore, that this pseudo-base is α-benzoylamino-γ-methyleneaminopropane (XIII), and that the salt is the hydrochloride of the isomeric benzoylhexahydropyrimidine (XIV):



Benzoyl-αγ-diamino-propane. (XII.)

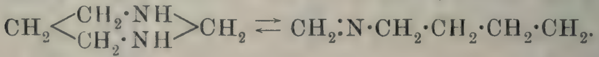
α-Benzoylamino-γ-methyleneaminopropane. (XIII.)

Benzoylhexahydropyrimidine hydrochloride. (XIV.)

The hydrochloride (XIV), unlike the dihydrochloride of hexahydropyrimidine, is quite stable, and rapidly crystallises in a pure form. This stability appears to be due to the fact that the hypothetical cyclic (pseudo) base is a strong one, and that its dissociation constant is much higher than the second dissociation constant of hexahydropyrimidine. With hexahydropyrimidine dihydrochloride some salt-hydrolysis takes place, yielding the monohydrochloride (IX), which at once comes into tautomeric equilibrium with the open-chain hydrochloride (VIII); the latter being sensitive to hydrogen ions, then suffers hydrolysis, as previously described.

## EXPERIMENTAL.

### *Hexahydropyrimidine and Methylene-αγ-diaminopropane,*



$$CH_2{<}\begin{matrix}CH_2\cdot NH\\ CH_2\cdot NH\end{matrix}{>}CH_2 \rightleftharpoons CH_2{:}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2.$$

The synthesis of this tautomeric compound was effected by the action of aqueous formaldehyde on αγ-diaminopropane monohydrochloride. An aqueous solution, of about 25 per cent. concentration, of the diamine, was divided in equal portions; one was neutralised exactly (using methyl-orange as indicator) with dilute ($N/10$) hydrochloric acid, and the other was then added. To the resulting aqueous solution of the monohydrochloride a solution of formaldehyde (1 mol.) of previously ascertained concentration was added very slowly drop by drop with continual agitation. Rapid action and disappearance of free formaldehyde took place at first, but as the rate of action fell off, care was taken to add the formaldehyde solution more slowly so as to avoid excess. The total time occupied in the addition was about an hour for 2·4 grams of αγ-diaminopropane hydrochloride. A clear, odourless solution resulted, which was neutral towards phenolphthalein, but alkaline towards litmus and methyl-orange. This solution consists essentially of the hydrochloride of methylene-αγ-diaminopropane. In the same way the acetate and oxalate were obtained from the corresponding mono-salts of αγ-diaminopropane.

*Isolation of the Free Base.*—The aqueous solution containing the hydrochloride was treated in the cold with solid potassium hydroxide in excess, when a colourless oil was precipitated, which was extracted with ether. The ethereal solution, after keeping for three hours over solid potassium hydroxide, on distilling, to remove the ether, left a light oil, but some of the base passed over with the ether. The light oil on fractionation gave a mobile, colourless distillate (about two-thirds of the total), boiling between 140° and 160°, and left a slightly discoloured syrup which began to darken above 220° without distilling. The volatile fraction was then immediately redistilled, and behaved in the same way as the original liquid, yielding a mobile liquid boiling between 140° and 160°, and leaving about the same proportion of non-volatile syrup. This syrup, evidently the polymerised form of methylene-$\alpha\gamma$-diaminopropane, fumed slightly in the air, and dissolved at once in water, yielding a strongly alkaline solution, which on benzoylation gave 1:3-dibenzoylhexahydropyrimidine, as an oil which solidified on keeping, and melting, after recrystallisation from aqueous alcohol, at 93°. A mixture with a specimen (1) obtained by benzoylation of the volatile fraction (see below), and (2) by benzoylation of methylene-$\alpha\gamma$-diaminopropane acetate (p. 334), melted at 93—94° in each case. In all other respects the aqueous solution of the syrup appeared to be identical with that of the volatile fraction; it yielded the same picrate mixture (p. 337), and showed the same behaviour on treatment with acid, as described below. The volatile fraction fumed strongly in the air, and possessed a peculiar basic odour and powerful basic properties. It was extremely hygroscopic, and on this account it was impossible to obtain an accurate analysis. After remaining for a short time over solid potassium it contained $N=29{\cdot}86$. On prolonged keeping over solid potassium hydroxide the mobile liquid gradually changes to a colourless, viscid syrup similar to that obtained by distillation. On passing air free from carbon dioxide, but containing minute traces of moisture, over the mobile liquid, water was taken up to the extent of about 1 molecular proportion, yielding apparently an ammonium hydroxide as a slightly syrupy liquid:

0·0756, by Kjeldahl's method, required 14·45 c.c. $N/10$-HCl. $N=26{\cdot}76$.

$C_4H_{10}N_2,H_2O$ requires $N=26{\cdot}90$ per cent.
$C_4H_{10}N_2$ requires $N=32{\cdot}56$ per cent.

An aqueous solution of the base on benzoylation by benzoyl chloride and alkali gave 1:3-dibenzoylhexahydropyrimidine, in needles melting, after recrystallisation from aqueous alcohol, at 94°, identical with the compound described above and on p. 339.

The behaviour of the base with dilute hydrochloric acid was investigated with the object of studying its tautomeric relations and hydrolysis; and attempts were also made to prepare a solid hydrochloride. An aqueous solution of the undistilled base was prepared by shaking the ethereal solution obtained as described on p. 335 with water, which very readily dissolves it. The concentration of this aqueous solution was ascertained by boiling with an excess of *N*/10-hydrochloric acid for thirty minutes, to hydrolyse it completely to trimethylenediamine, and titrating back the excess of acid. As 1 c.c. of this solution after hydrolysis required 4·5 c.c. of N/10-hydrochloric acid, corresponding with two basic nitrogen atoms, it follows that 1 c.c. of this solution should require 4·5 c.c. of *N*/10-hydrochloric acid if on neutralisation it gave hexahydropyrimidine dihydrochloride entirely, and 2·25 c.c. of *N*/10-hydrochloric acid if it gave the hydrochloride of methylene-αγ-diaminopropane entirely. Since 1 c.c. of this solution (0·225 molar concentration) at 21° required 2·5 c.c. of *N*/10-hydrochloric acid, using methyl-orange, to reach the first neutral point, it follows that the latter corresponds with a proportion of about 89 per cent. of the open-chain hydrochloride and 11 per cent. of the cyclic monohydrochloride in the equilibrium mixture. The effect of further gradual addition of hydrochloric acid to this neutral solution is to give an acid solution, which becomes neutral, rapidly at first, but more slowly as the second neutral point, which corresponds with the addition of about 2 c.c. of *N*/10-hydrochloric acid, is neared. The second neutral point thus corresponds with two equivalents of hydrochloric acid, combined partly with hexahydropyrimidine and partly with αγ-diaminopropane hydrolytically formed.

The effect on the second neutral point of excess (more than one equivalent) of acid on keeping was examined at 21° by adding 1 c.c. of the above aqueous solution of the base to varying amounts of *N*/10-hydrochloric acid, and titrating back after known intervals of time with *N*/10-sodium hydroxide. Similar experiments were made with *N*/10-sulphuric acid.

It was found that excess of acid, instead of accelerating the rate at which the second neutral point approaches that corresponding with the neutralisation of two equivalents, retards it. This point is, in fact, most rapidly attained when the base is gradually treated with acid so as to avoid appreciable excess of the latter. Attempts were made to ascertain the extent of hydrolysis by benzoylation, after keeping with acid for varying lengths of time. In no case, however, could any dibenzoyl-αγ-diaminopropane be obtained, and always 1:3-dibenzoylhexahydropyrimidine resulted, but this fact, which at first suggested that no hydrolysis had occurred, might be due to the recombination of αγ-diaminopropane and formaldehyde occurring during the Schotten-Baumann process. Moreover, free formaldehyde was shown by the well known colour tests, but it was not found possible to utilise these tests quantitatively. An attempt roughly to gauge the extent of hydrolysis was next made by evaporating solutions, obtained from the base by addition of hydrochloric acid, at laboratory temperatures, in a vacuum over potassium hydroxide and sulphuric acid, and fixing the composition of the resulting solid by analysis. In all cases the solid proved to be a mixture containing αγ-diaminopropane dihydrochloride. An odour of formaldehyde was also detected, showing that hydrolysis had occurred.

The following values showing the percentage of chlorine in the solid were obtained:

| | | |
|---|---|---|
| (1) | After evaporation with one equivalent of HCl.. ...... | Cl = 33·39 |
| (2) | ,, ,, ,, ,, HCl......... | Cl = 32·96 |
| (3) | ,, ,, with two equivalents of HCl ...... | Cl = 45·56 |
| (4) | ,, ,, ,, ,, HCl ...... | Cl = 46·41 |

(1) and (2) Methylene-αγ-diaminopropane hydrochloride requires Cl = 28·98 per cent.

αγ-Diaminopropane monohydrochloride requires Cl = 32·13 per cent.

(3) and (4) Hexahydropyrimidine dihydrochloride requires Cl = 44·67 per cent.

αγ-Diaminopropane dihydrochloride requires Cl = 48·29 per cent.

Solids 1 and 2 on extracting with alcohol, in which methylene-αγ-diaminopropane hydrochloride and αγ-diaminopropane monohydrochloride are soluble, left a considerable residue (48 per cent.) of insoluble αγ-diaminopropane dihydrochloride. (Found: (1) Cl = 47·79; (2) Cl = 47·33. Calc., Cl = 48·29 per cent.)

It follows from these analytical data that considerable hydrolysis had taken place (to the extent of 30 per cent. in 3 and to a further extent in the others), but forty-eight hours had elapsed during the evaporation. An attempt was next made to precipitate the dihydrochloride of hexahydropyrimidine by adding excess of alcoholic hydrogen chloride to a concentrated solution of the monoacetate of the base obtained as described on p. 334. A white, crystalline solid separated, which contained Cl = 47·17 per cent. This corresponds with a mixture of 30 per cent. of hexahydropyrimidine dihydrochloride and 70 per cent. of αγ-diaminopropane dihydrochloride, and on benzoylation it yielded a considerable quantity of dibenzoyl-αγ-diaminopropane (m. p. 146°). All attempts to prepare any pure salt of hexahydropyrimidine have so far failed. The *picrate* was obtained on adding aqueous picric acid to a solution of the base as a yellow, microcrystalline precipitate, melting at

186° to a turbid liquid. It was insoluble in water or alcohol, and was evidently a mixture of the mono- and di-picrates:

0·0756 gave 14·10 c.c. $N_2$ (moist) at 21° and 764 mm. N = 21·38.
Methylene-$\alpha\gamma$-diaminopropane picrate requires N = 22·22 per cent.
Hexahydropyrimidine dipicrate requires N = 20·59 per cent.
An equimolecular mixture requires N = 21·19 per cent.

### *α-Benzoylamino-γ-methyleneaminopropane,* $CH_2{:}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH\cdot COPh$.

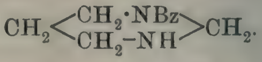
This compound in a polymerised form was obtained from monobenzoyl-$\alpha\gamma$-diaminopropane (T., 1912, **101**, 2350) by condensation with formaldehyde. One gram of the normal oxalate of this base, dissolved in the minimum quantity of water, was treated with one equivalent of *N*/10-sodium hydroxide, and the calculated quantity of formaldehyde was gradually added to the clear aqueous solution. A colourless oil was immediately precipitated, which was extracted with pure ethyl acetate. The solution, after remaining a short time over solid potassium hydroxide, was then evaporated and kept in a vacuum for several days. A clear oil remained, which gradually changed to a practically solid, transparent, glassy, amorphous, and brittle mass, weighing 0·72 gram (theory requires 0·85 gram), which showed no tendency to crystallise:

0·1130, by Kjeldahl's method, required 11·7 c.c. *N*/10-HCl. N = 14·58.

$C_{11}H_{14}ON_2$ requires N = 14·74 per cent.

The amorphous solid is insoluble in water, very soluble in alcohol, moderately so in benzene, sparingly so in ether, and insoluble in light petroleum. On heating with excess of water for several hours it slowly passes into solution, with hydrolysis, forming a clear, alkaline solution containing monobenzoyl-$\alpha\gamma$-diaminopropane and formaldehyde, which can be detected by its odour. On cooling, recombination takes place, α-benzoylamino-γ-methyleneaminopropane being precipitated as an emulsion. On treatment with cold water and phenolphthalein, it shows a perfectly neutral reaction, but it immediately dissolves in acids, with rearrangement, forming salts of benzoylhexahydropyrimidine.

### *Benzoylhexahydropyrimidine,*



$$CH_2{<}\begin{matrix}CH_2\cdot NBz\\ CH_2-NH\end{matrix}{>}CH_2.$$

The free base is unknown, and on liberation from its salts by alkali, undergoes immediate reverse rearrangement to the above open-chain isomeride, which is obtained as an insoluble oil. The *hydrochloride*, obtained by exact neutralisation by aqueous hydrochloric acid of α-benzoylamino-γ-methyleneaminopropane in aqueous alcoholic solution, on evaporation in a vacuum, crystallises in colourless needles, sparingly soluble in alcohol:

0·0843 gave 0·0534 AgCl. Cl = 15·68.

$C_{11}H_{14}ON_2,HCl$ requires Cl = 15·67 per cent.

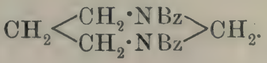
The *platinichloride* is precipitated slowly from dilute aqueous solution in clusters of orange needles, melting and decomposing at 202—203°:

0·1634 gave 0·0410 Pt. Pt = 25·09.

$(C_{11}H_{14}ON_2,HCl)_2PtCl_4$ requires Pt = 25·06 per cent.

The *picrate* and *oxalate* could not be obtained crystalline. The *acetate* slowly crystallises on evaporation in air.

### 1:3-*Dibenzoylhexahydropyrimidine*,



$$CH_2<\begin{matrix}CH_2\cdot NBz\\ CH_2\cdot NBz\end{matrix}>CH_2.$$

Attempts to obtain this compound, by the Schotten-Baumann benzoylation of α-benzoylamino-γ-methyleneaminopropane, failed apparently because of the highly insoluble polymerised nature of the latter, and only benzoic anhydride resulted.

The compound, however, was easily obtained in the wet benzoylation of the mixed bases (methylene-αγ-diaminopropane and hexahydropyrimidine) as already described (p. 335). It was most conveniently prepared direct from either the hydrochloride or acetate of the open-chain base obtained (p. 334) by the action of formaldehyde on the mono-salt of αγ-diaminopropane. On merely shaking with benzoyl chloride and alkali a 97 per cent. yield of the dibenzoyl derivative was obtained as an oil, which set to a crystalline solid on keeping. On recrystallisation from aqueous alcohol it formed coarse, transparent, colourless needles, melting at 95°:

0·1582 gave 12·9 c.c. $N_2$ (moist) at 16° and 756 mm. N = 9·46.

0·3331, by Kjeldahl's method, required 22·48 c.c. *N*/10-HCl. N = 9·45.

0·3025, by Kjeldahl's method, required 20·38 c.c. *N*/10-HCl. N = 9·43.

$C_{18}H_{18}O_2N_2$ requires N = 9·52 per cent.

The same compound was prepared by the condensation of formaldehyde and dibenzoyl-αγ-diaminopropane, the latter being dissolved in sufficient concentrated hydrochloric acid and treated with an excess of 40 per cent. formaldehyde. After six days the solution was diluted and left, when the compound slowly crystallised in needles (m. p. 94°), and a further crop (m. p. 93°) was obtained by neutralising the acid mother liquor with alkali; the total yield was 75 per cent. of the theoretical.

1:3-*Dibenzoylhexahydropyrimidine* is insoluble in water or light petroleum, very soluble in alcohol, acetone, acetic acid, or chloroform; sparingly so in cold benzene, ether, or carbon tetrachloride, and moderately so in hot benzene. It is moderately soluble in cold concentrated hydrochloric acid or 98 per cent. sulphuric acid, without decomposition. It is slowly hydrolysed by heating with aqueous mineral acids, yielding benzoic acid, formaldehyde, and αγ-diaminopropane, which was identified as its dibenzoyl derivative. The hydrolysis is incomplete with concentrated hydrochloric acid at 80° in seven and a-half hours, but complete after heating a further two hours at 100°. On boiling with 10 per cent. sodium hydroxide, two molecules of benzoic acid are eliminated, and methylene-αγ-diaminopropane, largely undecomposed, is produced; on benzoylating the product after complete hydrolysis a good yield of the original compound is obtained.

Organic Laboratory,
University of Liverpool.

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## XLII.—*The Interaction of Bromine and the Sulphides of β-Naphthol. Part II.*

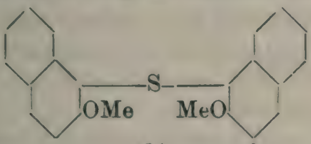
By Thomas Joseph Nolan and Samuel Smiles.

In the first part of this investigation (T., 1912, **101**, 1420) it was shown that with bromine the stable sulphide of β-naphthol yields 1:6-dibromo-β-naphthol, sulphur being displaced by the halogen, whilst the unstable sulphide yields a derivative of dibromonaphthasulphonium-quinone. Thence the inference was made that the hydroxy- and thio-groups of the unstable sulphide respectively occupy positions 2 and 1 in the naphthalene nucleus which are the same as those occupied in the stable sulphide. Moreover, since the halogen in the bromonaphthasulphonium-quinone is situated in the quinonoid portion of the naphthalene nucleus, it is of some importance to determine whether this substitution by halogen takes place before or after conversion to the quinonoid structure, for in the former circumstance valuable information with regard to the structure of the unstable sulphide would be at hand.

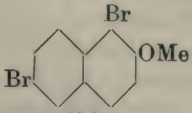
The experiments described in the following pages were originally undertaken with this end in view, and accordingly the interaction of bromine and the acyl and alkyl derivatives of the two sulphides has been examined with the hope that with these derivatives of the unstable sulphide substitution would take place without other disturbance.

### *Derivatives of the Stable Sulphide.*

The methyl ether of β-naphthol sulphide (I) was obtained by the interaction of sulphur chloride and the methyl ether of β-naphthol:



(I.)



(II.)

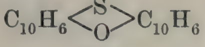
Other means of obtaining this substance were employed with unsatisfactory results, and the experience met with serves as further illustration (*loc. cit.*) of the ease with which the stable sulphide of β-naphthol loses sulphur from the α-position; thus methylation with methyl sulphate in alkaline solution proceeds very sluggishly, and if the conditions are intensified sulphur is partly eliminated in the form of methyl sulphide and other products. Also, when the silver salt of β-naphthol sulphide is treated with methyl iodide, the interaction is complex; partial oxidation to the sulphonium-quinone takes place whilst methyl sulphide is abundantly formed. However, the method first described furnishes excellent yields of the required substance.

When this methyl ether is suspended in cold glacial acetic acid and treated with eight atomic proportions of bromine, a rapid interaction takes place, and the methyl ether of 1:6-dibromo-β-naphthol (II) is formed in almost quantitative yield whilst sulphur is eliminated. The acetyl derivative of β-naphthol sulphide exhibits considerably greater stability towards this reagent than the methyl ether, for when it is suspended in a cold solution of bromine in acetic acid scarcely any interaction takes place even during the lapse of six or seven hours. Also, when a cold solution of this acetyl derivative in acetic anhydride is treated with bromine, the greater portion of the compound ultimately separates unchanged from the medium. Comparison of this behaviour of the acetyl derivative of the stable sulphide with that of the acetylated unstable sulphide shows an emphatic contrast.

### *Derivatives of the Unstable Sulphide.*

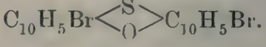
Henriques (*Ber.*, 1894, **27**, 2999) has stated that the acetyl derivative of the unstable sulphide may be obtained as a yellow, crystalline material, which melts at 148°. Presumably the method which yielded this substance was the same as that employed in preparing the acetyl derivative of the stable sulphide, namely, prolonged treatment with acetic anhydride and sodium acetate. On repeating this experiment we have found that a substance of this appearance and approximate melting point is formed, but on further examination this has proved to be the anhydride of the unstable sulphide. The substance is dealt with in a subsequent paragraph, and it is sufficient for the present to mention that the required acetyl derivative is a colourless, amorphous substance which is readily obtained from the interaction of the unstable sulphide and cold acetic anhydride in the presence of camphorsulphonic acid.

The chief characteristic of this acetyl derivative is the instability of the acyl groups, which are very easily eliminated; thus, for example, treatment with boiling acetic anhydride and sodium acetate under suitable conditions converts the acetyl derivative into the anhydride (III) of the unstable sulphide (P., 1912, **28**, 275):



$$C_{10}H_6<^{S}_{O}>C_{10}H_6$$

(III.)

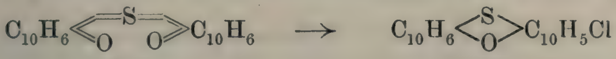


$$C_{10}H_5Br<^{S}_{O}>C_{10}H_5Br.$$

(IV.)

This substance (III) may also be obtained by the action of other dehydrating agents on the unstable sulphide, and since the latter contains the thio-arrangement and two hydroxyl groups (see p. 346 and T., 1912, **101**, 1420) the formula shown above is assigned to the anhydride, which is provisionally termed *iso*naphthathioxin. Moreover, it may be noticed that although the substance differs in physical character from the naphthathioxin (m. p. 166°) obtained from the stable sulphide (Mauthner, *Ber.*, 1906, **39**, 1340), the chemical characteristics of the two anhydrides are closely similar; thus both yield sulphoxides when treated with nitric acid or thioxonium salts by addition of bromine; the former give chloro-derivatives by reaction with hydrogen chloride, and the latter are converted into bromo-derivatives by heating with certain solvents. A more detailed account and comparison of the two anhydrides and their derivatives will be given in a subsequent paper.

When the anhydride of the unstable sulphide is treated with excess of bromine (at least four atomic proportions) an insoluble, green thioxonium bromide is formed, which on being heated in certain solvents yields the dibromo-derivative (IV) of the *iso*naphthathioxin. In the formula by which this substance is represented, a bromine atom is assigned to each naphthalene nucleus; it seems highly probable that this arrangement is correct, but no direct proof of it can at present be brought forward. The acetyl derivative of the unstable sulphide by treatment with excess of bromine (eight atomic proportions) in cold acetic acid also is converted into a green thioxonium bromide, which easily yields a dibromonaphthathioxin identical with that obtained by direct bromination of *iso*naphthathioxin. It is therefore clear that with this reagent the acetyl groups are very easily removed from diacetylnaphthol *iso*sulphide, and the contrast with the behaviour of diacetylnaphthol sulphide clearly shows a profound difference in the structure of these two substances. The result obtained with the acetyl derivative of the unstable sulphide is sufficiently striking to warrant a brief discussion of the probable mechanism of the process. Previous experiments (T., 1912, **101**, 715) have shown that $\beta$-naphthasulphonium-quinone (V) is easily attacked by acetyl chloride, yielding the monochloronaphthathioxin (VI); and on



$$C_{10}H_6\genfrac{}{}{0pt}{}{\ll}{}\overset{S}{\genfrac{}{}{0pt}{}{}{O\quad O}}\genfrac{}{}{0pt}{}{\gg}{}C_{10}H_6 \longrightarrow C_{10}H_6<\genfrac{}{}{0pt}{}{S}{O}>C_{10}H_5Cl$$

(V.) (VI.)

substituting acetyl bromide for the chloride we find that a similar product is obtained. The interaction is not so rapid as with the chloride, and the product is a mixture of the mono- and dibromonaphthathioxins which is difficult completely to resolve; but after further bromination the pure dibromonaphthathioxin (IV) was isolated. Moreover, the same substance (IV) is obtained by interaction of excess of bromine and the naphthasulphonium-quinone (V) in cold acetyl bromide or acetic anhydride.

On comparing the behaviour of the unstable sulphide with that of its diacetyl derivative, it is seen that with excess of bromine in cold acetic acid the former gives the dibromonaphthasulphonium-quinone (T., 1912, **101**, 1420; also experimental part of this paper), whilst the latter yields the dibromonaphthathioxin. This apparent anomaly can only be explained by the production of naphthasulphonium-quinone in both cases at a preliminary stage of the interaction:

$$C_{20}H_{12}S(OH)_2 + Br_2 = O{:}C_{10}H_6{:}S{:}C_{10}H_6{:}O + 2HBr.$$
$$C_{20}H_{12}S(OAc)_2 + Br_2 = O{:}C_{10}H_6{:}S{:}C_{10}H_6{:}O + 2AcBr.$$

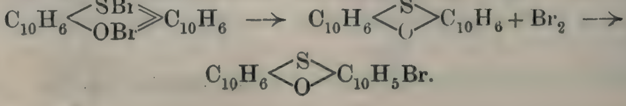
It is then evident that in the former case merely further bromination will take place; but in the latter acetylbromide is formed simultaneously with the quinone, and, as already mentioned, it may be shown by independent experiment that under these conditions with excess of bromine the quinone yields the dibromonaphthathioxin (IV). Further confirmation of this conclusion is afforded by the fact that the unstable sulphide when treated with this halogen in acetic anhydride yields the same naphthathioxin derivative.

Thus it may be inferred that in these interactions the quinone is formed before bromination takes place. Moreover, it is necessary to mention that if the reverse were correct the dibromosulphonium-quinone should result, for experiment shows that under the conditions adopted this substance is not converted by bromine and acetic anhydride into the dibromonaphthathioxin. For these reasons it must be admitted that the position taken up by the halogen in the dibromosulphonium-quinone or the dibromonaphthathioxin cannot be legitimately employed as evidence in a discussion of the nature of the unstable sulphide, for it seems, as already pointed out, that these are formed by bromination of the quinone under different conditions. It is, on the other hand, very clear from these experiments that the two sulphides remarkably differ from one another in the character of the hydroxyl groups which they contain.

In summarising the results of these experiments which have dealt with the interaction of bromine and the isomeric sulphides of $\beta$-naphthol or their acetyl derivatives, it may be stated that the stable sulphide, the methyl ether, and the acetyl derivative are evidently true derivatives of $\beta$-naphthol. On the other hand, it is clear that the unstable sulphide cannot be so regarded; indeed, the hydroxyl groups exhibit the peculiar character of certain unsaturated tertiary alcohols. This question will be more fully discussed when more complete evidence of the character of the substance has been obtained from a study of the *iso*naphthathioxin mentioned in the foregoing pages.

It remains finally to remark that in all these cases where bromination of the naphthathioxin takes place in presence of an excess of the halogen an insoluble thioxonium bromide is formed at the penultimate stage, but the substance may be converted by heat, either in the reacting mixture or separately, into the dibromonaphthathioxin. Unfortunately, this bromide is sufficiently unstable to defy attempts to obtain it in a condition fit for analysis, for, after being freed from excess of bromine and during desiccation, it partly loses bromine and partly undergoes further bromination in the nuclei. A mixture of mono- and di-bromonaphthathioxins is then obtained, in which the former greatly predominates. When heated with some inactive medium the latter change supervenes, and the chief product is the dibromo-derivative.

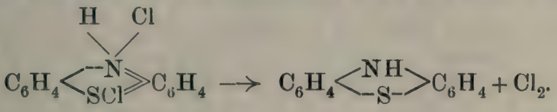
It seems, therefore, that in the conversion of the thioxonium salt into the bromonaphthathioxins separation of the halogen takes place before bromination of the nucleus, for example:



$$C_{10}H_6{<}\substack{SBr\\OBr}{\geqslant}C_{10}H_6 \longrightarrow C_{10}H_6{<}\substack{S\\O}{>}C_{10}H_6+Br_2 \longrightarrow C_{10}H_6{<}\substack{S\\O}{>}C_{10}H_5Br.$$

Regarded independently, this conclusion is of little importance, but it throws some light on the analogous case of the interaction of phenazothionium chloride and hot hydrogen chloride.

The products here obtained (Page and Smiles, T., 1910, **97**, 1112) are mono- and di-chlorothiodiphenylamine, and the fact that the mixture is produced is sufficient to indicate that the process is not a simple intramolecular change. It has been observed (*loc. cit.*) that the presence of hydrogen chloride is indispensable to the reaction, and the behaviour of the thioxonium salts now recorded lends further weight to the hypothesis that the final chlorination



$$C_6H_4{<}\genfrac{}{}{0pt}{}{\overset{H\quad Cl}{-N-}}{SCl}{>}C_6H_4 \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{-S-}{>}C_6H_4 + Cl_2.$$

(VII.)

is due to the separation of halogen from the dichloride (VII) of the phenazothionium base.

## EXPERIMENTAL.

### *Derivatives of the Stable Sulphide.*

*The Dimethyl Ether*, $MeO\cdot C_{10}H_6\cdot S\cdot C_{10}H_6\cdot OMe$.—A solution of sulphur dichloride in dry chloroform was gradually added to a cold concentrated solution of two molecular proportions of β-naphthol methyl ether in the same solvent. Interaction took place at once, hydrogen chloride being rapidly evolved, and after the mixture had been kept at the atmospheric temperature for three hours the required substance had almost completely separated in the crystalline state. The yield of the crude product obtained in this manner was almost quantitative. It was recrystallised from a large volume of boiling acetone, and after being dried was analysed:

0·1019 gave 0·2841 $CO_2$ and 0·0492 $H_2O$. C = 76·0; H = 5·3.

$C_{22}H_{18}O_2S$ requires C = 73·3; H = 5·2 per cent.

The *dimethyl ether* of *β-naphthol sulphide* forms pale yellow needles, which melt at 184°, and are sparingly soluble in most cold organic media. Like the hydroxy-derivative, it readily dissolves in concentrated sulphuric acid, giving an intensely blue solution.

*Reaction with Bromine.*—The finely powdered substance was added to a cold solution of eight atomic proportions of bromine in cold glacial acetic acid. The mixture was kept at the atmospheric temperature, and shaken at frequent intervals. The sulphide gradually dissolved, and after the lapse of about three hours, when solution was complete, the reacting liquid was poured into a large bulk of water, the solid precipitate being subsequently collected.

The product was recrystallised from alcohol, and, by a close comparison with the product of methylation of 1:6-dibromo-β-naphthol (Davis, T., 1900, **77**, 37) or of bromination of β-naphthyl methyl ether, was identified as the methyl ether of 1:6-dibromo-β-naphthol. It melted at 100°, whether heated alone or mixed with the substance obtained from these sources.

### *Diacetyl Derivative*, $AcO{\cdot}C_{10}H_6{\cdot}S{\cdot}C_{10}H_6{\cdot}OAc$.

This substance has been described by Henriques (*Ber.*, 1894, **27**, 2990), who obtained it by acetylating the dihydroxy-compound with acetic anhydride in presence of sodium acetate. The preparation may be more efficiently carried out by heating to 80° the hydroxysulphide with acetic anhydride and a small quantity of camphorsulphonic acid. Experiments were made on the behaviour of this substance with bromine under the same conditions as adopted in the treatment of the acetyl derivative of the unstable sulphide. The finely powdered substance was suspended in cold glacial acetic acid, and treated with eight atomic proportions of bromine. No definite interaction could be detected, for, after the reacting mixture had been kept for one hour at the atmospheric temperature with frequent agitation, almost the whole of the original acetyl derivative was recovered unchanged. Further, a warm solution of this acetyl derivative in acetic anhydride was mixed with eight atomic proportions of bromine, and when this was set aside the greater portion of the original material separated unchanged. It will be seen from experiments described in subsequent paragraphs that the behaviour of the acetyl derivative of the unstable sulphide is profoundly different; this substance is immediately attacked by the reagent under the same conditions.

### *Derivatives of the Unstable Sulphide.*

Evidence showing the presence of two hydroxyl groups in the unstable sulphide has already been adduced by Henriques (*loc. cit.*), who prepared and analysed the lead salt of this substance. Further data supporting this conclusion have now been obtained by estimating the active hydrogen available for reaction with magnesium methyl iodide (Hibbert and Sudborough, P., 1904, **19**, 285; Zerewetinoff, *Ber.*, 1907, **40**, 2023; 1908, **41**, 2233):

0·0730 gave 10·03 c.c. $CH_4$ at 0° and 760 mm. OH = 10·76.

$C_{20}H_{12}S(OH)_2$ requires OH = 10·69 per cent.

The same conclusion is furnished by the existence of a diacetyl derivative.

*Diacetyl Derivative of the Unstable Sulphide.*—The acetyl derivative of this sulphide has been described by Henriques (*loc. cit.*, p. 3002) as occurring in yellow needles which melt at 148°. The method of preparing this substance was not described, but it seems probable that the process employed was that of prolonged heating with acetic anhydride and sodium acetate which was used in obtaining the acetyl derivative of the stable sulphide. Applying this method we have obtained a substance approximately agreeing with that mentioned by Henriques, but it is the anhydride of the hydroxy-derivative, and is apparently formed by secondary decomposition of the required acetyl compound.

The latter substance is not easily obtained in the pure condition, but after many trials we find that the best method is as follows:

Five grams of the sulphide were suspended in 70 c.c. of cold acetic anhydride, and 1 gram of camphorsulphonic acid was added to the mixture. The sulphide gradually dissolved, and after the mixture had been kept at the atmospheric temperature for four hours acetylation was complete. The reacting liquid was decomposed with ice-cold water; then the insoluble acetyl derivative was collected and purified by precipitating with water from the cold alcoholic solution. The latter operation must be cautiously effected, otherwise the substance may separate in an oily mass; also it may be observed that the success of the preparation largely depends on the purity of the sulphide employed. The product thus obtained is a colourless, amorphous solid, which liquefies at about 75°; on cooling it re-solidifies to a colourless, glass-like material. For analysis it was dried at 100°:

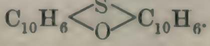
0·1188 gave 0·3100 $CO_2$ and 0·0478 $H_2O$. C = 71·2; H = 4·4.

$C_{24}H_{18}O_4S$ requires C = 71·6; H = 4·4 per cent.

On hydrolysis with acids and subsequent distillation of the mixture, the substance yielded acetic acid. It is immediately attacked by cold alcoholic ammonia, and from the alkaline liquid the stable sulphide of β-naphthol was obtained. The formation of the latter compound is to be expected, for the unstable sulphide is converted into the stable by alkaline reagents. Another substance insoluble in aqueous alkaline media was isolated from this interaction, but it has not yet been further examined.

The diacetyl derivative is readily soluble in most organic media and insoluble in water.

### *Anhydride of the Unstable Sulphide or* iso*Naphthathioxin*,



$$C_{10}H_6<\substack{S\\O}>C_{10}H_6.$$

A solution of 5 grams of the acetate of the unstable sulphide and 5 grams of freshly fused sodium acetate in about 75 c.c. of acetic anhydride was boiled under reflux. The solution gradually assumed a yellow colour, and heating was continued until a sample yielded a semi-crystalline mass on treatment with water. The maximum yield is usually attained after about seventeen hours; more prolonged heating is not advisable, since further decomposition then occurs, and the product is more difficult to isolate. After a suitable period the reacting liquid was allowed to cool, when a mixture of the required substance with sodium acetate separated in the crystalline state. This was collected, and the sodium acetate removed by washing with water. The yield of the crude product thus obtained varied from about 80 per cent. in one experiment to about 10 per cent.; that usually obtained was about 40 per cent., but the most favourable conditions have not yet been definitely ascertained. The substance was purified by crystallisation from glacial acetic acid, with the addition of animal charcoal if necessary; it was then obtained in lemon-yellow needles, which melted at 152°:

0·1086 gave 0·3172 $CO_2$ and 0·0394 $H_2O$. C=79·66; H=4·0.

$C_{20}H_{12}OS$ requires C=80·00; H=4·0 per cent.

It may be recalled that dehydration of the stable sulphide of β-naphthol yields naphthathioxin (Mauthner, *Ber.*, 1906, **39**, 1340; Christopher and Smiles, T., 1912, **101**, 713), which melts at 166°. This is not the same as the substance now described; in fact, a mixture of the two in approximately equal quantities melts indefinitely at about 120°; moreover, each substance furnishes a distinct series of derivatives (P., 1912, **28**, 275). However, in their chemical nature the two anhydrides resemble one another very closely; indeed, so far as experiment has yet been carried, no clear distinction of this kind has been observed. The substance now described has therefore been termed *iso*naphthathioxin; a fuller investigation of the two series will be soon completed.

The mother liquors from this preparation were examined, and found to contain a further small quantity of the anhydride, the bulk of the dissolved material being the unchanged acetyl derivative. In some experiments a very small quantity of the acetyl derivative of the stable sulphide was isolated and identified in the usual manner. The occurrence of this substance is of some interest, for it seems to show that the unstable acetylated sulphide may be partly transformed into the stable one by the action of heat; whilst the only other means of passing from the unstable to the stable sulphide hitherto recorded is by the influence of alkali hydroxide.

### *Dibromo*iso*naphthathioxin*, $C_{10}H_5Br{<}\begin{smallmatrix}S\\O\end{smallmatrix}{>}C_{10}H_5Br$.

(*a*) *From* iso*Naphthathioxin.*—A solution of the anhydride of the unstable sulphide in warm glacial acetic acid was mixed with rather more than four atomic proportions of bromine. The sparingly soluble thioxonium salt was at once precipitated, but on boiling the liquid it was rapidly converted into a mass of yellow needles. These were collected and purified by crystallisation from hot carbon tetrachloride, when *dibromo*iso*naphthathioxin* was obtained in a mass of yellow, thread-like crystals, which melted at 245°:

0·1015 gave 0·1943 $CO_2$ and 0·0214 $H_2O$. C = 52·2; H = 2·3.
0·1325 „ 0·1088 AgBr. Br = 34·9.

$C_{20}H_{10}OBr_2S$ requires C = 52·4; H = 2·18; Br = 34·9 per cent.

The substance is very sparingly soluble in most cold organic media, and moderately so in hot tetrachloroethane or acetic anhydride. When warmed with concentrated sulphuric acid, it gives a green solution—a colour reaction which is characteristic of this series. The same substance may be readily obtained by several other methods, of which the following are brief descriptions:

(*b*) *By Interaction of Bromine and the Acetyl Derivative of the Unstable Sulphide.*—A solution of 5 grams of the acetyl derivative in cold glacial acetic acid was gradually mixed with eight atomic proportions of bromine. The precipitated thioxonium salt was collected, and after being freed from excess of bromine by washing with cold acetic acid, it was treated with the boiling medium. When conversion into the yellow bromo-derivatives was complete, the liquid was cooled and the insoluble, crystalline material was collected. By fractional crystallisation from boiling acetic acid a less soluble portion was obtained, and this was found to be dibromo*iso*naphthathioxin (m. p. 245°); it was identical with the substance formed by bromination of *iso*naphthathioxin. The more soluble part of the product melted at about 176°; analysis showed that this substance consisted chiefly of the monobromonaphthathioxin, but this was contaminated with the dibromo-derivative, which could not be completely removed from the small quantity of material available. Further bromination (see later paragraph) of this substance yielded the pure dibromo-derivative. When the thioxonium bromide obtained in this interaction is treated with boiling acetic acid bromine is liberated, and it seems probable that loss of halogen in this manner may lead to the formation of a small quantity of the monobromo-derivative. If the salt is kept in a vacuous desiccator for twenty-four hours, conversion into the bromonaphthathioxins takes place, whilst bromine is liberated. Under these conditions the amount of the dibromo-derivative formed is relatively smaller, and that of the monobromo-compound is relatively larger, but also in this case complete purification of the latter substance was not attained.

It may be mentioned that this difficulty experienced in obtaining the more soluble halogen derivative in a pure condition from a mixture of two has been previously met with in the mono- and di-chloro-derivatives of thiodiphenylamine (Unger and Hofmann, *Ber.*, 1896, **29**, 1362; Page and Smiles, T., 1910, **97**, 1116).

The yield of the bromonaphthathioxins from 5 grams of the acetyl derivative was about 2 grams, but this may be greatly improved by substituting acetic anhydride for acetic acid as the medium for bromination.

(*c*) *By Interaction of Bromine and the Unstable Sulphide.*—Previous experiments have shown that the unstable sulphide reacts with bromine in acetic acid, yielding the dibromosulphonium-quinone (T., 1912, **101**, 1420); but if acetic anhydride is employed as the solvent the bromonaphthathioxins are exclusively formed. The conditions adopted and the results obtained were precisely similar to those described in the foregoing paragraphs.

(*d*) *By Interaction of Bromine and Naphthasulphonium-quinone.* Five grams of the quinone were suspended in 50 c.c. of cold acetic anhydride, and eight atomic proportions of bromine were slowly added to the mixture. On the first addition of bromine the quinone rapidly dissolved, and subsequently the contents of the flask solidified to a mass of the green thioxonium bromide. A dibromonaphthathioxin, identical with that previously described, was isolated from this salt by the process already mentioned. The yield of the crude bromo-derivative was approximately equal in weight to the quinone taken. The interaction of β-naphthasulphonium-quinone and four atomic proportions of bromine in glacial acetic acid has been previously investigated (Nolan and Smiles, *loc. cit.*), and it was found that a tribromo-derivative is formed, from which the dibromosulphonium-quinone may be obtained by removal of hydrogen bromide. The unstable sulphide with six atomic proportions of the halogen gave the same products. Since the present experiments with larger quantities of halogen and acetic anhydride as the solvent have yielded entirely different products, it was necessary to repeat the former experiments with glacial acetic acid, using the larger excess of halogen. However, the same results were obtained, the dibromonaphthasulphonium-quinone (Found, C=50·4, H=2·2, Br=33·6. Calc., C=50·6, H=2·1, Br=33·7 per cent.) being formed either from the quinone or from the unstable sulphide. A correction in the melting point of this substance must be made, from the 193° formerly given to 213° obtained with a sample recrystallised from acetic anhydride. Moreover, it must also be observed that the temperature of decomposition of the tribromo-derivative, which forms the initial product of the interaction, may vary considerably according to the mode of purification, although the data of analysis remain in accord with theory. Whether this behaviour is due to the presence of slight impurities or to the presence of isomeric tribromo-derivatives is at present uncertain, but the same quinone was obtained from the many different samples examined.

*Interaction of Naphthasulphonium-quinone and Acetyl Bromide.*—When the quinone is added to cold acetyl bromide it is readily attacked; the material dissolves, forming a brown solution. Further interaction does not begin until the mixture has been warmed on the water-bath, when the bromo-derivatives of naphthathioxin are gradually precipitated in the crystalline state. Heating was continued for one hour before the product was isolated by filtration from the cooled mother liquors; the yield was very poor, about 0·7 gram being obtained from every 5 grams of the quinone taken. Analysis showed that the product (m. p. 178°) consisted of monobromonaphthathioxin mixed with a small quantity of the dibromo-derivative. Attempts to obtain either substance in the pure condition were not successful, and hence for identification the substance was treated with excess of bromine in glacial acetic acid. The pure dibromo-derivative thus obtained was identical with that formed in the other various reactions described in this paper.

The Organic Chemistry Laboratory,
University College, London.

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## XLIII.—*Researches on the Constitution of Physostigmine. Part II. The Synthesis of 3-Dimethylaminoacetyl-2-methylindole and 2-α-Dimethylamino-γ-hydroxypropylindole.*

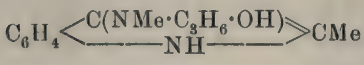
By Arthur Henry Salway.

Previous investigations on the constitution of physostigmine (eserine), $C_{15}H_{21}O_2N_3$, have shown that the principal degradation product of the alkaloid is eseroline, $C_{13}H_{18}ON_2$, this substance being derived from the parent compound by alkaline hydrolysis with elimination of carbon dioxide and methylamine, according to the equation:

$$C_{13}H_{17}ON_2\cdot CO\cdot NHMe + H_2O = C_{13}H_{18}ON_2 + CO_2 + NH_2Me.$$

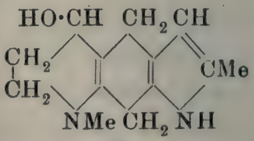
The solution of the problem of the constitution of physostigmine thus depends on the determination of the constitution of eseroline. The investigation of the latter was recently undertaken by the present author (T., 1912, **101**, 978), who showed that this substance is in all probability an indole derivative, since it yields 2-methylindole when distilled with zinc dust in a current of hydrogen. Moreover, it was also shown that eseroline is a tertiary monacid base containing a methyl group attached to nitrogen, that it possesses weakly acid properties, and that it rapidly absorbs oxygen in the presence of alkalis with the formation of rubreserine, eserine-blue, and other oxidation products. Whilst this knowledge concerning the properties of eseroline and its degradation products is insufficient to enable the author to propose a constitution for the alkaloid with a reasonable degree of certainty, it nevertheless seemed desirable for the purpose of the present investigation to construct a hypothetical formula which would serve as a basis for some synthetical experiments.

In the construction of such a formula it is evident that the methylindole complex, which eseroline presumably contains, will account for the group of atoms $C_9H_9N$, the nitrogen atom of which will correspond with the non-basic nitrogen atom of eseroline. The remaining part of the molecule, $C_4H_9ON$, will contain a tertiary basic nitrogen atom attached to a methyl group, and also, in all probability, a hydroxyl group,* and may therefore be further resolved into the group $C_3H_5(OH)(NMe)$. The nature of the union between the indole complex and the group $C_3H_5(OH)(NMe)$ now remains to be considered. In the first place, the latter might be in combination with the indole nucleus as an aliphatic side-chain, in which case eseroline would be represented by a formula of the type I:



$$C_6H_4{<}\begin{array}{c}C(NMe\cdot C_3H_6\cdot OH)\\ \hline NH\end{array}{>}CMe$$

(I.)



(II.)

On the other hand, there exists the possibility that the group, $C_3H_5(OH)(NMe)$, forms a closed chain with the indolic part of the molecule. In this case the simplest formula which can be constructed in agreement with the known properties of eseroline is of the type II.

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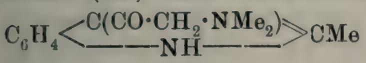
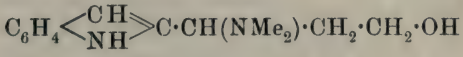
* The presence of a hydroxyl group in eseroline is probable, but has not been established beyond question.

The author has now undertaken the synthesis of compounds belonging to the types I and II in the hope of obtaining more definite knowledge regarding the constitution of eseroline. In the present investigation two derivatives of indole containing a basic and oxygenated side-chain, namely, 3-*dimethylaminoacetyl*-2-*methylindole* (III) and 2-α-*dimethylamino*-γ-*hydroxypropylindole* (IV),



$$C_6H_4{<}\begin{matrix}C(CO\cdot CH_2\cdot NMe_2)\\ NH\end{matrix}{>}CMe$$

(III.)



$$C_6H_4{<}\begin{matrix}CH\\ NH\end{matrix}{>}C\cdot CH(NMe_2)\cdot CH_2\cdot CH_2\cdot OH$$

(IV.)

have been prepared, and their properties compared with those of eseroline. It has been found that these synthetic compounds possess properties which differ greatly from those of eseroline, and it may therefore be concluded that the latter is not a simple substituted indole of the type represented by formula I.

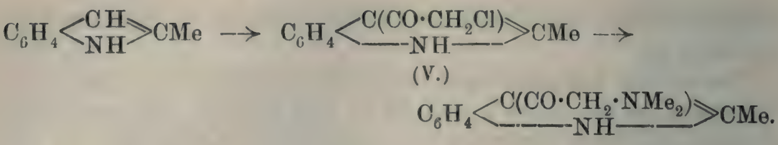
It is proposed in subsequent investigations to attempt the synthesis of compounds of the kind represented by formula II.

A number of general methods are known for the synthesis of substituted indoles, but whilst a few of these can be applied with good results in the preparation of the simpler indole derivatives, none of them appears to be of much service in the preparation of indoles with an extended side-chain. Recently, however, Oddo (*Gazzetta*, 1911, **41**, i, 234) has indicated the possibility of preparing indoles, substituted in the 3-position, by the aid of the Grignard reaction, whilst Madelung (*Ber.*, 1912, **45**, 1128, 3541) has found that *o*-toluidides may be converted into substituted indoles by heating with sodium ethoxide at a high temperature. These methods have now been used by the author for the preparation of the indole compounds described in the present investigation.

## EXPERIMENTAL.

### I.—*Synthesis of* 3-*Dimethylaminoacetyl*-2-*methylindole* (III).

Oddo has shown (*loc. cit.*) that indole reacts with magnesium methyl iodide with the formation of magnesium indolyl iodide, which by subsequent treatment with acetyl chloride yields 3-acetylindole. In the present experiments a similar process has been employed for the conversion of 2-methylindole into 3-chloroacetyl-2-methylindole, which then yielded 3-dimethylaminoacetyl-2-methylindole on treatment with dimethylamine. These changes are represented in the following scheme:



$$C_6H_4{<}\begin{matrix}CH\\NH\end{matrix}{>}CMe \longrightarrow C_6H_4{<}\begin{matrix}C(CO\cdot CH_2Cl)\\NH\end{matrix}{>}CMe \longrightarrow$$

(V.)

$$C_6H_4{<}\begin{matrix}C(CO\cdot CH_2\cdot NMe_2)\\NH\end{matrix}{>}CMe.$$

### 3-*Chloroacetyl-2-methylindole* (V).

For the preparation of this compound two parts of magnesium powder were mixed with nine parts of ethyl bromide in the presence of dry ether. After the magnesium had completely dissolved, eleven parts of 2-methylindole, dissolved in dry ether, were added drop by drop, and the mixture kept at the ordinary temperature for about an hour. Chloroacetyl chloride (nine parts), dissolved in ether, was then slowly added in the cold. At first the addition of the latter caused the precipitation of a viscid, yellow solid, which finally became cherry-red. After all the chloroacetyl chloride had been added, the upper layer of ethereal liquid was decanted, and the viscid solid which remained was agitated vigorously with an aqueous solution of sodium hydrogen carbonate, when an almost colourless solid, insoluble in the alkaline liquid, was obtained. This was collected, dried, and crystallised several times from ethyl acetate, from which it was deposited in slender, colourless needles, melting at 220°:

0·0830 gave 0·1946 $CO_2$ and 0·0380 $H_2O$. C=63·9; H=5·1.
0·1286 „ 0·0876 AgCl. Cl=16·9.
$C_{11}H_{10}ONCl$ requires C=63·6; H=4·8; Cl=17·1 per cent.

3-*Chloroacetyl-2-methylindole* is sparingly soluble in ether, benzene, or chloroform, but more readily so in alcohol or ethyl acetate. Its chlorine atom is very reactive, being quickly removed when heated with alkalis, and also to some extent when heated with alcohol.

In one experiment for the preparation of the above compound magnesium methyl iodide was employed in the place of magnesium ethyl bromide with a somewhat unexpected result. The product of the reaction in this case was a mixture of two compounds in approximately equal proportions. One of these compounds was the desired 3-chloroacetyl-2-methylindole melting at 220°, whilst the other melted at 197°, and did not contain chlorine. The latter substance on analysis gave the following figures:

0·1075 gave 0·3011 $CO_2$ and 0·0642 $H_2O$. C=76·4; H=6·6.
$C_{11}H_{11}ON$ requires C=76·3; H=6·4 per cent.

It appeared probable from this result that the compound melting at 197° possessed the constitution $C_6H_4{<}\begin{matrix}CAc\\NH\end{matrix}{>}CMe$, and had been formed in the above reaction by the reducing action of the liberated hydriodic acid on the 3-chloroacetyl-2-methylindole. If this supposition regarding the constitution of the compound melting at 197° were correct, then the same substance should be obtained by the action of acetyl chloride on magnesium 2-methylindolyl iodide. This experiment, conducted in a manner similar to that employed in the preparation of 3-chloroacetyl-2-methylindole, yielded a product identical with the above-mentioned substance melting at 197°. The latter is therefore 3-acetyl-2-methylindole.

3-*Acetyl-2-methylindole* is moderately soluble in chloroform or alcohol, but only sparingly so in benzene or ether. It crystallises from hot alcohol in slender, colourless needles, and from chloroform in thin, colourless plates, melting at 197°. It does not give the pine-shaving colour reaction of indole. It yields an *oxime*, which crystallises from dilute alcohol in glistening leaflets, melting and decomposing at 199°:

0·0972 gave 0·2502 $CO_2$ and 0·0568 $H_2O$. C=70·2; H=6·5.

$C_{11}H_{12}ON_2$ requires C=70·2; H=6·4 per cent.

### 3-*Dimethylaminoacetyl-2-methylindole* (III).

A quantity of 3-chloroacetyl-2-methylindole was heated for four hours at 100° in a sealed tube with an excess of dimethylamine dissolved in alcohol. The solvent and the excess of dimethylamine were first removed in a current of steam, and the mixture then acidified with dilute hydrochloric acid, when a quantity of non-basic material remained undissolved, the latter being collected and set aside for subsequent examination. The acid liquid was now made alkaline with sodium carbonate, and the precipitated base collected, washed with water, and purified by crystallisation from alcohol. It was obtained in colourless, rhombohedral prisms, which melted at 201°. The yield of pure substance amounted to 62 per cent. of the theoretical:

0·0958 gave 0·2540 $CO_2$ and 0·0640 $H_2O$. C=72·3; H=7·4.

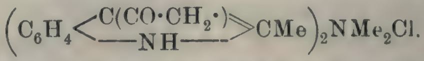
$C_{13}H_{16}ON_2$ requires C=72·2; H=7·4 per cent.

The non-basic by-product in the above reaction was very sparingly soluble in the usual organic solvents. It was crystallised, however, from much hot acetic acid, and then obtained in small, colourless, square prisms, which melted and decomposed at 270°:

0·1304 gave 0·3243 $CO_2$ and 0·0760 $H_2O$. C=67·8; H=6·5.
0·1980 „ 0·0640 AgCl. Cl=8·0.
0·1718 „ 14·4 c.c. $N_2$ at 12° and 775 mm. N=10·2.

$C_{24}H_{26}O_2N_3Cl$ requires C=68·0; H=6·1; N=9·9; Cl=8·4 per cent.

It appears from these results and the properties of the compound that the latter is a quaternary ammonium salt formed by the union of one molecule of 3-dimethylaminoacetyl-2-methylindole and one of 3-chloroacetyl-2-methylindole, and therefore has the constitution:



$$\left(C_6H_4<\begin{array}{c}C(CO\cdot CH_2\cdot)\\ NH\end{array}>CMe\right)_2NMe_2Cl.$$

3-*Dimethylaminoacetyl-2-methylindole* is sparingly soluble in ether, chloroform, or benzene, and moderately so in alcohol. It is a stable base, showing no tendency to absorb oxygen in the presence of alkalis. It does not respond to the pine-shaving test for indoles. Its *hydrochloride*, prepared by dissolving the base in dilute hydrochloric acid, evaporating the solution to dryness and crystallising the residue from alcohol, was obtained in colourless, rhombohedral crystals, melting at 258°.

Many attempts were made to reduce the above base in order to obtain from it by the addition of two atoms of hydrogen a substance of the same empirical formula as eseroline, but reduction could not be effected; thus, when the base was heated with tin and hydrochloric acid, or with sodium in amyl alcohol, no change occurred, whilst treatment with hydriodic acid and red phosphorus at 120° caused disruption of the molecule with formation of 2-methylindole.

### II.—*Synthesis of* 2-*α-Dimethylamino-γ-hydroxypropylindole* (IV).

As already indicated, Madelung (*loc. cit.*) has shown that *o*-toluidides may be converted into substituted indole derivatives by heating with sodium ethoxide. Although this reaction has hitherto only been applied to the *o*-toluidides of acetic, benzoic, and oxalic acids, it appeared probable that the method might be extended to the preparation of any indole derivative, $C_6H_4<\begin{array}{c}CH\\ NH\end{array}>\mathbf{CR}$, provided that the acid $R\cdot CO_2H$ could be obtained. For the purpose of the present synthesis the radicle R was required to consist of an oxygenated acyl group containing a tertiary basic nitrogen atom, and the corresponding acid, $R\cdot CO_2H$, chosen as best fitted to meet these requirements, was α-dimethylamino-γ-hydroxybutyric acid,

$$HO\cdot CH_2\cdot CH_2\cdot CH(NMe_2)\cdot CO_2H.$$

The steps which were necessary for the preparation of this compound and for its conversion into the desired indole derivative are as follows:

$$CH_2Br\cdot CH_2Br \longrightarrow \underset{\text{(VI.)}}{PhO\cdot CH_2\cdot CH_2Br} \longrightarrow \underset{\text{(VII.)}}{PhO\cdot CH_2\cdot CH_2\cdot CH(CO_2H)_2}$$

$$\longrightarrow \underset{\text{(VIII.)}}{PhO\cdot CH_2\cdot CH_2\cdot CBr(CO_2H)_2} \longrightarrow \underset{\text{(IX.)}}{PhO\cdot CH_2\cdot CH_2\cdot CHBr\cdot CO_2H} \longrightarrow$$

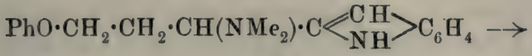
$$\underset{\text{(X.)}}{PhO\cdot CH_2\cdot CH_2\cdot CH(NMe_2)\cdot CO_2H} \text{ and}$$

$$\mathrm{PhO{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me} \longrightarrow$$

(XI.)

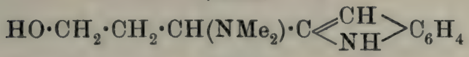
$$\mathrm{PhO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}CO{\cdot}NH{\cdot}C_6H_4Me} \longrightarrow$$

(XII.)



$$\mathrm{PhO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}C}{\ll}\begin{smallmatrix}\mathrm{CH}\\ \mathrm{NH}\end{smallmatrix}{>}\mathrm{C_6H_4} \longrightarrow$$

(XIII.)



$$\mathrm{HO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}C}{\ll}\begin{smallmatrix}\mathrm{CH}\\ \mathrm{NH}\end{smallmatrix}{>}\mathrm{C_6H_4}$$

(XIV.)

The compounds represented by the formulæ (VI) and (VII) in the above scheme have already been described by Perkin, Bentley, and Haworth (T., 1896, **69**, 169), whilst the compounds (VIII) and (IX) have been synthesised by Fischer (*Ber.*, 1907, **40**, 106).

### *a-Dimethylamino-γ-phenoxybutyric Acid* (X).

For the preparation of this compound one part of *a*-bromo-γ-phenoxybutyric acid, obtained from ethylene dibromide as described by the above-mentioned investigators (*loc. cit.*), was heated in a sealed tube for six hours at 100° with two parts of an aqueous solution (33 per cent.) of dimethylamine. The product was then distilled in a current of steam with a known amount of sodium hydroxide until the excess of dimethylamine had been removed. A quantity of hydrobromic acid equivalent in amount to the sodium hydroxide employed was then added, and the liquid concentrated to dryness under diminished pressure. The residue was then digested with absolute alcohol, the alcoholic liquid filtered to remove the sodium bromide, and the filtrate evaporated. The amino-acid was thus obtained as a viscid oil, which did not crystallise on keeping. When agitated with a little aqueous hydrobromic acid, however, it immediately solidified, with the formation of a crystalline hydrobromide. This was purified by recrystallisation from water, and was then obtained in colourless, thin plates, melting at 86°:

0·1183 (air-dried), heated at 110°, lost 0·0124 $H_2O$. $H_2O = 10·5$.
0·1445 „ gave 0·0784 AgBr. Br = 23·1.
$C_{12}H_{18}O_3NBr,2H_2O$ requires $H_2O = 10·6$; Br = 23·5 per cent.
0·1059 * gave 0·1824 $CO_2$ and 0·0562 $H_2O$. C = 47·0; H = 5·9.
$C_{12}H_{18}O_3NBr$ requires C = 47·4; H = 5·9 per cent.

In order to obtain the free base, the above-described hydrobromide was dissolved in water, and an amount of sodium carbonate added just sufficient to combine with the hydrobromic acid. The mixture was then evaporated to dryness under diminished pressure, and the amino-acid extracted from the residue by means of absolute alcohol. After evaporating the alcoholic extract, the amino-acid was obtained as a very hygroscopic, amorphous solid, which could not be obtained crystalline.

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* Anhydrous substance.

*α-Dimethylamino-γ-phenoxybutyric acid* (X) is readily soluble in alcohol or water, insoluble in ether, benzene, or chloroform. It yields a *hydrochloride*, which crystallises from water in prismatic needles melting at 83°. The *methyl* ester of the latter,

$$PhO\cdot CH_2\cdot CH_2\cdot CH(CO_2Me)\cdot NMe_2,HCl,$$

crystallises from hot ethyl acetate in colourless aggregates of flat plates, which melt at 130°:

0·1000 gave 0·2086 $CO_2$ and 0·0666 $H_2O$. C=56·9; H=7·4.

$C_{13}H_{19}O_3N,HCl$ requires C=57·0; H=7·3 per cent.

For the next stage in the synthesis it was necessary to prepare the *o*-toluidide of the above-described amino-acid (XII). Attempts were first made to obtain this compound from the acid chloride, $PhO\cdot CH_2\cdot CH_2\cdot CH(NMe_2)\cdot COCl$, but the latter could not be prepared. Ultimately the difficulty was overcome by first preparing the *o*-toluidide of α-bromo-γ-phenoxybutyric acid (XI), and subsequently displacing the bromine in this compound by the dimethylamino-group.

### *α-Bromo-γ-phenoxybutyro-o-toluidide* (XI).

Seven parts of α-bromo-γ-phenoxybutyric acid were dissolved in ether, and six parts of phosphorus pentachloride added. After the reaction had subsided, the ether, together with the phosphoryl chloride which had been formed, was removed on the water-bath under diminished pressure, and the residual crude acid chloride then added to an excess of *o*-toluidine dissolved in ether. A voluminous precipitate of the *o*-toluidide was thus formed, which was collected, washed with water, and recrystallised from hot alcohol, when it separated in colourless, prismatic needles, melting at 147°:

0·1000 gave 0·2145 $CO_2$ and 0·0478 $H_2O$. C=58·5; H=5·3.

$C_{17}H_{18}O_2NBr$ requires C=58·6; H=5·2 per cent.

*α-Bromo-γ-phenoxybutyro-o-toluidide* is only moderately soluble in ether, but more readily so in chloroform, ethyl acetate, or alcohol.

### *α-Dimethylamino-γ-phenoxybutyro-o-toluidide* (XII).

This substance was prepared by heating the foregoing compound in a sealed tube at 100° for two hours with an excess of dimethylamine dissolved in alcohol. The alcohol and excess of dimethylamine were then removed in a current of steam, when the required base was precipitated as a colourless oil. This was dissolved in ether, the ethereal solution dried, and the solvent removed. The residual oil slowly solidified, and was then purified by crystallisation from light petroleum, when it separated in radiating clusters of colourless, prismatic needles, melting at 54°:

0·1265 gave 0·3376 $CO_2$ and 0·0898 $H_2O$. C = 72·8; H = 7·9.

$C_{19}H_{24}O_2N_2$ requires C = 73·1; H = 7·7 per cent.

*α-Dimethylamino-γ-phenoxybutyro-o-toluidide* is very readily soluble in the usual organic solvents, and can only be crystallised with difficulty. It is a weak base, forming salts which are acid towards litmus, and also possess an extremely bitter taste. The *hydrochloride*, prepared by passing a current of dry hydrogen chloride into an ethereal solution of the base, crystallises from a mixture of alcohol and ethyl acetate in slender, colourless needles, melting at 169°:

0·1010 gave 0·2410 $CO_2$ and 0·0646 $H_2O$. C = 65·1; H = 7·1.

$C_{19}H_{24}O_2N_2,HCl$ requires C = 65·4; H = 7·2 per cent.

The *platinichloride* of the above base crystallises from alcohol, containing a little hydrochloric acid, in small, brown prisms, melting at 215°.

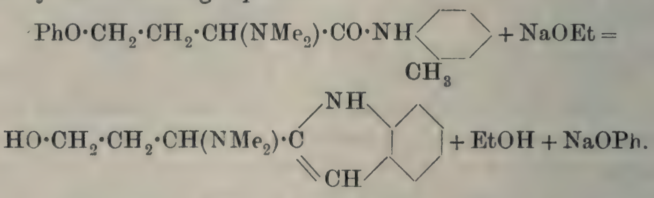
### 2-*α-Dimethylamino-γ-hydroxypropylindole.*

In order to prepare this compound 0·3 gram of sodium was dissolved in absolute alcohol in a capacious flask, and the alcohol removed under diminished pressure; to the sodium ethoxide thus obtained, 2 grams of α-dimethylamino-γ-phenoxybutyro-*o*-toluidide were added, and the mixture heated in a metal bath to a temperature of 250—300° in a current of hydrogen. At this temperature reaction took place with effervescence and a considerable darkening in colour, and the process was soon complete. The entire operation was repeated four times with the same quantities of material, and the products from the several reactions were then united and acidified with dilute hydrochloric acid. The acid liquid was next shaken with ether, which removed a considerable quantity of phenol, identified by means of its tribromo-derivative, then made alkaline with sodium carbonate, and the mixture repeatedly extracted with chloroform. The chloroform extracts were washed, dried, and the solvent removed, when an oily, basic residue was obtained, which did not crystallise on keeping. For its purification it was dissolved in dilute hydrochloric acid, the solution evaporated to dryness under diminished pressure, and the solid residue thus obtained crystallised from a mixture of alcohol and ethyl acetate. The hydrochloride of the base then separated in colourless, prismatic needles, melting at 218°. The amount of pure hydrochloride obtained from 10 grams of the *o*-toluidide was 3·3 grams:

0·0962 gave 0·2166 $CO_2$ and 0·0646 $H_2O$. C=61·4; H=7·5.

$C_{13}H_{18}ON_2,HCl$ requires C=61·3; H=7·5 per cent.

It is evident from this result that the sodium ethoxide in the above reaction has not only effected the expected indolic condensation, but has also simultaneously removed the phenyl group with the formation of 2-α-dimethylamino-γ-hydroxypropylindole, as represented by the following equation:



*2-α-Dimethylamino-γ-hydroxypropylindole.*—The pure base was prepared from the above-described hydrochloride by treating the latter with aqueous sodium carbonate, and extracting the alkaline liquid with chloroform; after the removal of the chloroform, the base was obtained as a colourless, volatile oil, which did not solidify in a freezing mixture. It was miscible with ether, chloroform, ethyl acetate, alcohol, or water:

0·0910 gave 0·2375 $CO_2$ and 0·0698 $H_2O$. C=71·2; H=8·5.

$C_{13}H_{18}ON_2$ requires C=71·6; H=8·3 per cent.

The *aurichloride* of the above base crystallises from dilute alcohol in yellow prisms, which melt at 133° and are anhydrous:

0·1140 gave 0·1174 $CO_2$, 0·0353 $H_2O$, and 0·0400 Au. C=28·1; H=3·4; Au=35·1.

$C_{13}H_{18}ON_2,HAuCl_4$ requires C=28·0; H=3·4; Au=35·3 per cent.

The *picrate* crystallises from dilute alcohol in spherical aggregates of bright yellow rhombs, which melt at 140°.

The base, 2-α-dimethylamino-γ-hydroxypropylindole, which has now been synthesised, is isomeric with the alkaloid eseroline. The properties of these two compounds are, however, very dissimilar, as a comparison shows: thus, eseroline in the presence of alkalis readily absorbs oxygen with the production of intensely coloured solutions, whilst the synthetic base is quite stable under similar conditions. Moreover, eseroline readily reduces gold and silver salts, and is also a strong base, which yields neutral salts. The synthetic base, on the other hand, possesses no reducing properties, and is a weak base yielding salts with a strongly acid reaction. The synthetic base, furthermore, differs considerably from eseroline in physiological action, as shown by some experiments kindly conducted by Dr.

H. H. Dale, director of the Wellcome Physiological Research Laboratories, to whom the author here wishes to express his best thanks: thus, on the one hand, eseroline was found to produce the characteristic myotic action of physostigmine (but in a diminished degree) when injected into the eye, and also to effect a slowing of the heart-beat after intravenous injection. The synthetic base, 2-α-dimethylamino-γ-hydroxypropylindole, on the other hand, possessed none of these physiological properties.

The Wellcome Chemical Research Laboratories,
London, E.C.

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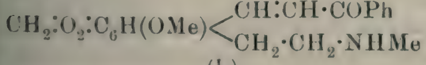
# XLIV.—*Synthetical Experiments in the Group of the* iso*Quinoline Alkaloids. Part III. The Constitution of Anhydrocotarnineacetophenone, etc., together with an Account of Some New Condensation Products of Cotarnine.*

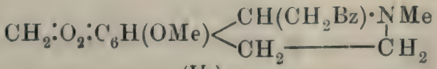
By Edward Hope and Robert Robinson.

At an early stage of this series of experiments (Part I., T., 1911, **99**, 1153; Part II., *ibid.*, 2114) it became evident that certain statements made by Liebermann and his co-workers with regard to the constitution of the condensation products of cotarnine with various substances were without satisfactory experimental foundation (Liebermann and Kropf, *Ber.*, 1904, **37**, 211; Liebermann and Glawe, *ibid.*, 2738; Kropf, *ibid.*, 2744). In the light of the explanation of the ready condensation of cotarnine with various nitro-compounds (T., *loc. cit.*, 2117), and, indeed, with a number of substances containing reactive hydrogen atoms, we have repeated some of these earlier experiments, and have examined particularly the cases of condensation with acetophenone and ethyl phenylacetate. Liebermann and Glawe recognised the possibility of two structures for the condensation products of cotarnine. Anhydrocotarnineacetophenone might be represented by (I) or (II), a derivative of *N*-methylaminoethylbenzaldehyde, or of *N*-methyltetrahydro*iso*quinoline respectively:



$$CH_2{:}O_2{:}C_6H(OMe)<\begin{matrix}CH{:}CH\cdot COPh\\ CH_2\cdot CH_2\cdot NHMe\end{matrix}$$

(I.)

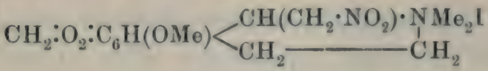


$$CH_2{:}O_2{:}C_6H(OMe)<\begin{matrix}CH(CH_2Bz)\cdot NMe\\ CH_2\text{———}CH_2\end{matrix}$$

(II.)

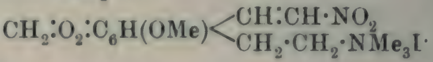
In this connexion Liebermann and Glawe say: "It is possible to discriminate between the two forms in various ways, especially by proving the presence of a hydrogen atom attached to nitrogen by methylation or acylation." Using such methods, they concluded that some condensation products had the structure corresponding with (I)—and here were classed all the condensation products of cotarnine with "active" methylene groups—whilst others had the structure (II).

If the above-mentioned methods were universally trustworthy, there would be little difficulty in determining the constitution of any of the condensation products in question. The present authors have, however, already described (T., 1911, **99**, 2120) the remarkable formation of a mixture of methiodides from anhydrocotarninenitromethane (a perfectly homogeneous substance which possesses the tetrahydro*iso*quinoline structure). These methiodides agree in properties and composition with the formulæ:



$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{array}{l}CH(CH_2\cdot NO_2)\cdot NMe_2I \\ CH_2\text{————}CH_2\end{array}$$

and



$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{array}{l}CH{:}CH\cdot NO_2 \\ CH_2\cdot CH_2\cdot NMe_3I\end{array}$$

and it therefore appears that methyl iodide may cause the partial transformation of the cyclic form of anhydrocotarninenitromethane into the open-chain form. A substance exhibiting similar properties to anhydrocotarninenitromethane is anhydrocotarnineacetophenone. It was observed by Kropf that the behaviour of this compound with methyl iodide varied with the experimental conditions, particularly the temperature; but these reactions were explained in accordance with the open-chain formula as follows: The reaction with methyl iodide in the cold (or in methyl-alcoholic solution) was supposed to occur thus:

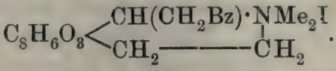
$$2C_{17}H_{13}O_4\cdot CH_2\cdot CH_2\cdot NHMe + 2MeI = C_{17}H_{13}O_4\cdot CH_2\cdot CH_2NMe_3I + C_{17}H_{13}O_4\cdot CH_2\cdot CH_2NHMe,HI,$$

whilst if the reaction was allowed to proceed without cooling, its course was represented thus:

$$C_{17}H_{13}O_4\cdot CH_2\cdot CH_2\cdot NHMe + MeI = C_{17}H_{13}O_4\cdot CH_2\cdot CH_2\cdot NMe_2,HI,$$

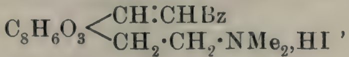
the sole product in this case being the hydriodide of methylanhydrocotarnineacetophenone.

Our experimental results agree in the main with those of Kropf, but we put forward the following interpretation, which we believe to be more satisfactory than that summarised above. Anhydrocotarnineacetophenone has the tetrahydro*iso*quinoline structure (II, p. 361), but is capable of reacting in the tautomeric form with reagents like benzoyl chloride and methyl iodide. When methyl iodide alone reacts with anhydrocotarnineacetophenone and the interaction is allowed to proceed without cooling, the cyclic structure remains intact and the methiodide,



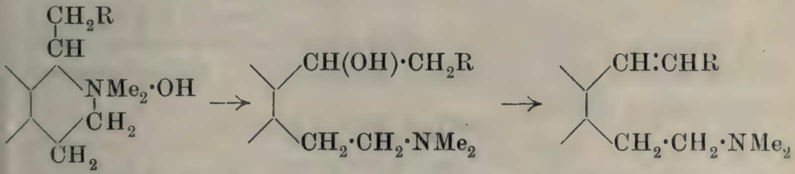
$$C_8H_6O_3\left<\begin{matrix}CH(CH_2Bz)\cdot NMe_2I\\ CH_2\text{————}CH_2\end{matrix}\right. .$$

melting at 180°, is produced. Kropf regarded this as the hydriodide of methylanhydrocotarnineacetophenone:



$$C_8H_6O_3\left<\begin{matrix}CH\colon CHBz\\ CH_2\cdot CH_2\cdot NMe_2,HI\end{matrix}\right. ,$$

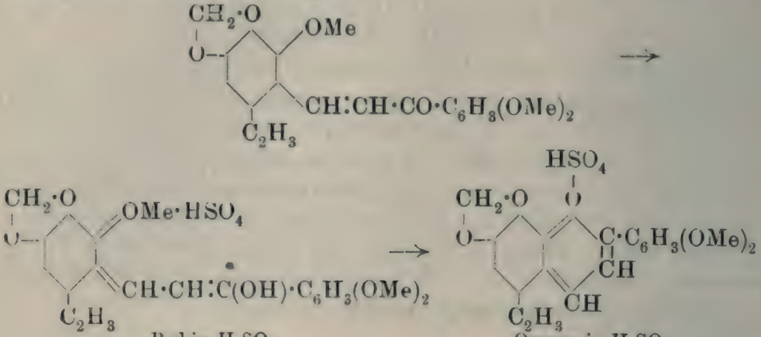
but the preparation of the latter by the action of hydriodic acid on methylanhydrocotarnineacetophenone showed the two substances to be totally different. Kropf's principal reason for believing this substance to be a hydriodide was that its aqueous solution gave an immediate precipitate of methylanhydrocotarnineacetophenone when treated with alkalis. This we regard as nothing more than the usual change which occurs when all similar derivatives of the quaternary ammonium salts of tetrahydro*iso*quinoline are treated with sodium hydroxide and potassium hydroxide:



Further, although, as mentioned above, anhydrocotarnineacetophenone yields a benzoyl derivative, it does not do so smoothly, and the difficulty of obtaining this derivative in good yield is very considerable. It is therefore believed that benzoyl chloride behaves like methyl iodide in causing the scission of the hydrocotarnine ring.

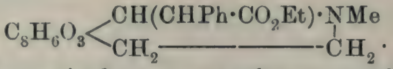
It is not easy to determine whether a minute amount of the open-chain form of anhydrocotarnineacetophenone exists in equilibrium with the cyclic form. If this be so, benzoyl chloride, which reacts only with the open-chain form, will progressively change the whole of the substance into this form, whilst methyl iodide, which reacts with both of the possible forms of anhydrocotarnineacetophenone, will only cause the conversion of a portion of this substance into the open-chain form. It is hoped to throw some light on this matter by the spectroscopic examination of a number of derivatives of substances allied in constitution to anhydrocotarnineacetophenone.

In connexion with the degradation of anhydrocotarnineacetophenone to cotarnonideneacetophenone by the Hofmann process, we found it necessary to synthesise the latter from cotarnone and acetophenone. The similarly constituted substance obtained from resacetophenonedimethyl ether exhibited an interesting behaviour on treatment with concentrated sulphuric acid. It dissolves in this reagent with the production of a red colour, which, however, quickly changes to orange. When the orange solution is poured into water, a solution of an oxonium salt is produced, as evidenced by the formation of a picrate and a platinichloride. These changes take place through the stages:



Red in $H_2SO_4$. Orange in $H_2SO_4$.

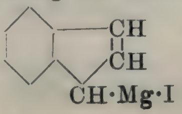
A complete examination of ethyl anhydrocotarninephenylacetate showed that it was constituted analogously to anhydrocotarnineacetophenone, namely:



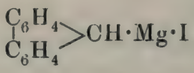
$$C_8H_6O_3<\begin{matrix}CH(CHPh\cdot CO_2Et)\cdot NMe\\ CH_2\text{———————}CH_2\end{matrix}\cdot$$

The cyclic structure is, however, vastly more stable. No trace of a benzoyl derivative could be obtained by vigorous treatment with benzoyl chloride, nor could a nitroso-compound be prepared.

At the end of the experimental portion of this paper are described some new condensation products of cotarnine with substances containing active hydrogen atoms, namely, 1-hydrindone, 1:3-diketohydrindene, indene, fluorene, isatin, and α-methylindole. Although the constitutional formulæ assigned to these substances have not as yet been experimentally founded, there can be little doubt regarding the correctness of the structure given in the experimental portion of the paper. The active hydrogen in some of the above-mentioned substances has been located by means of magnesium methyl iodide; for example, indene and fluorene yield one molecule of methane in each case, forming magnesium derivatives having the constitutions:

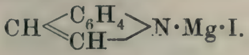


and



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>CH\cdot Mg\cdot I$$

respectively. In the case of α-methylindole it is highly probable that the most reactive hydrogen atom is that attached to the nitrogen, as in indole itself, Oddo (*Gazzetta*, 1911, **41**, i, 221) having shown that the product of the interaction of the latter with magnesium methyl iodide possesses the constitution:

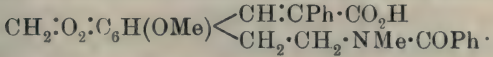


$$\mathrm{CH}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CH}\end{matrix}{>}\mathrm{N{\cdot}Mg{\cdot}I.}$$

It is a curious fact that it has so far been found impossible to condense cotarnine with diphenylamine or carbazole, although these compounds show the presence of active hydrogen by their behaviour towards Grignard reagents, as well as by their formation of potassium compounds.

## Experimental.

### *Benzoylanhydrocotarninephenylacetic Acid,*



$$\mathrm{CH_2{:}O_2{:}C_6H(OMe)}{<}\begin{matrix}\mathrm{CH{:}CPh{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CH_2{\cdot}NMe{\cdot}COPh}\end{matrix}{\cdot}$$

This acid was prepared in order to obtain evidence bearing on the constitution of ethyl anhydrocotarninephenylacetate. A mixture of benzoylcotarnine (13 grams), sodium phenylacetate (16 grams), and acetic anhydride (26 grams) was heated at 130—135° (temperature regulated) for three days.

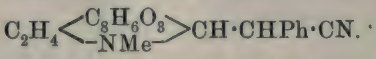
The product was poured into hot water and washed with several changes to remove acetic anhydride and sodium acetate. The oil was then shaken with sodium carbonate and ether, and the aqueous layer separated and acidified with concentrated hydrochloric acid. The yellow precipitate was collected and crystallised from aqueous alcohol. It was obtained in small, colourless, lozenge-shaped plates, melting at 205—206°, which were dried in a vacuum over sulphuric acid:

0·1263 gave 0·3262 $CO_2$ and 0·0592 $H_2O$. C = 70·4; H = 5·2.
0·2587 „ 7·5 c.c. $N_2$ at 22° and 764 mm. N = 3·3.
$C_{27}H_{25}O_6N$ requires C = 70·6; H = 5·4; N = 3·1 per cent.

This acid is of remarkable stability, and although many attempts were made to hydrolyse it they were quite fruitless, since the acid was usually recovered unchanged. Unlike most substances derived from cotarnine this acid can be heated to 280° without decomposition. The double linking appears to be sterically affected, since a solution of the acid in sodium carbonate does not decolorise potassium permanganate in the cold, nor does the substance take up bromine with any readiness (compare p. 369).

Since we were unable to hydrolyse the benzoyl compound we attempted to benzoylate ethyl anhydrocotarnine phenylacetate, but this substance behaves differently from anhydrocotarnineacetophenone (see p. 369), and no trace of a benzoyl derivative could be isolated.

### *Anhydrocotarninephenylacetonitrile,*



$$C_2H_4{<}\genfrac{}{}{0pt}{}{C_8H_6O_3}{-NMe-}{>}CH\cdot CHPh\cdot CN.$$

A solution of cotarnine (10 grams) and phenylacetonitrile (5 grams) in methyl alcohol (20 c.c.) was allowed to remain at the room temperature. The condensation product, which separated after half an hour, was collected, washed with methyl alcohol, and crystallised from ethyl acetate. The substance occurs in large, colourless prisms, readily soluble in hot ethyl acetate, but sparingly so in methyl or ethyl alcohols. It begins to decompose at 135°, and melts to a red liquid at 153—155°:

0·1467 gave 0·3859 $CO_2$ and 0·0800 $H_2O$. C=71·7; H=6·0.
$C_{20}H_{20}O_3N_2$ requires C=71·4; H=5·9 per cent.

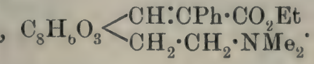
The formation of the red substance, obtained when the compound is fused, is also observed when the solution of the nitrile in solvents of high boiling point, for example, xylene, are boiled, and this reaction is highly characteristic.

The substance shows the usual reactions associated with its basic character, and is decomposed by hot acetic acid, with the production of cotarnine and phenylacetonitrile.

*Methylanhydrocotarninephenylacetonitrile Picrate.*—Anhydrocotarninephenylacetonitrile was mixed with methyl sulphate, when reaction occurred with evolution of heat, and the product was a colourless, crystalline methosulphate, which was dissolved in hot water and treated with excess of sodium hydroxide. The resulting colourless oil could not be solidified, and was therefore dissolved in ether, and, after evaporation of the dried ethereal solution, dissolved in alcohol and mixed with an alcoholic solution of picric acid. The *picrate* of the base separated in bright yellow prisms, and was recrystallised from ethyl alcohol, in which it is sparingly soluble in the cold. The crystals are clusters of prismatic needles of highly characteristic shape, and melt at 169—170° without decomposition:

0·1525 gave 16·0 c.c. $N_2$ at 13° and 758 mm. N=12·4.
$C_{21}H_{22}O_3N_2,C_6H_3O_7N_3$ requires N=12·1 per cent.

### *Ethyl 2-Methoxy-3:4-methylenedioxy-6-β-dimethylaminoethyl-α-phenylcinnamate*,



$$C_8H_6O_3\begin{cases}CH{:}CPh{\cdot}CO_2Et\\CH_2{\cdot}CH_2{\cdot}NMe_2\end{cases}.$$

In preparing ethyl anhydrocotarninephenylacetate * Liebermann and Glawe (*Ber.*, 1904, **37**, 2738) employed sodium carbonate as condensing agent, but we have found that a good yield may be obtained by simply mixing cotarnine with ethyl phenylacetate in molecular quantities in cold alcohol. The ester was heated on the steam-bath with an excess of methyl iodide, and in the course of about fifteen minutes the contents of the flask became quite solid owing to the separation of the methiodide. The excess of methyl iodide was removed by distillation, and the residue crystallised from alcohol. Six grams of the pure substance are obtained from 5 of the ester. The compound forms long, faintly yellow prisms, melting at 173—174°:

0·1151 gave 0·2203 $CO_2$ and 0·0605 $H_2O$. C=52·2; H=5·8.

0·1112 „ 0·0493 AgI. I=24·0.

$C_{23}H_{28}O_5NI$ requires C=52·6; H=5·4; I=24·0 per cent.

The methiodide (2·6 grams) was dissolved in a little hot water, and warmed on the steam-bath with precipitated silver chloride (1 gram) for three-quarters of an hour. The silver iodide was then separated by filtration from the aqueous solution of the methochloride, to which *N*-sodium hydroxide (7 c.c.) was added. The precipitated oil was extracted with ether, the ethereal solution dried, and distilled, leaving an uncrystallisable residue. The substance was, however, obtained in a sufficiently pure condition for analysis by dissolving the oil in dilute hydrochloric acid and extracting the basified solution with ether. The viscid oil remaining after evaporation of the ether and long exposure to a vacuum was analysed:

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* It is curious that two substances have been isolated by crystallisation of the picrates of both ethyl anhydrocotarninephenylacetate and its methohydroxide.

*Ethyl Anhydrocotarninephenylacetate Picrates.*

The mixture of substances is obtained as a yellow precipitate when picric acid is added to a solution of the substance in dilute hydrochloric acid. On crystallisation from methyl alcohol the first fraction consists of hexagonal plates melting at 124—126°, and is produced in considerable quantity, whilst the second fraction is obtained in long rods which melt at 138—142°.

*Ethyl anhydrocotarninephenylacetate methohydroxide picrates* are obtained by the addition of aqueous picric acid to a solution of the corresponding methiodide. On fractional crystallisation from methyl alcohol the first crop consists of plates and melts at 119—120°, whilst the second and larger fraction also crystallises in plates, differs characteristically in that crystals evolve solvent of crystallisation at 110—114°, resolidify, and then melt at 162—163°. We have not yet accumulated sufficient data to enable us to determine the nature of these substances.

0·1582 gave 0·3977 $CO_2$ and 0·0958 $H_2O$. C=68·5; H=6·7.

$C_{23}H_{27}O_5N$ requires C=69·5; H=6·8 per cent.

The agreement is as close as can be expected for an uncrystallised substance.

The colourless solution of the base in concentrated hydrochloric acid gives, on the addition of water, a precipitate which redissolves in excess.

*The Picrate.*—The solution of the base in dilute acid was treated with aqueous picric acid, when a bright yellow picrate was obtained, and after separation the derivative was crystallised from methyl alcohol. It was so obtained in magnificent, yellow prisms, melting at 195—196°:

0·2100 gave 0·4256 $CO_2$ and 0·0923 $H_2O$. C=55·3; H=4·8.

$C_{23}H_{27}O_5N,C_6H_3O_7N_3$ requires C=55·6; H=4·8 per cent.

*The Platinichloride.*—When platinic chloride is added to a solution of the base in dilute hydrochloric acid, an almost colourless precipitate is obtained. The substance was purified to a certain extent by boiling with a large quantity of water, and after drying melted at 208—209°:

0·1171 gave 0·0189 Pt. Pt=16·1.

$(C_{23}H_{27}O_5N)_2H_2PtCl_6$ requires Pt=16·2 per cent.

*The Methiodide.*—An excess of methyl iodide was poured on the oily base, when a vigorous reaction took place almost immediately; the temperature reached the boiling point of methyl iodide in a few seconds, and a crystalline solid was produced. After stirring the mixture, the excess of methyl iodide was evaporated, and the residue, a white solid, crystallised from methyl alcohol. The glistening, colourless prisms which separated melted at 197° with some change at 183°, probably evolution of solvent of crystallisation:

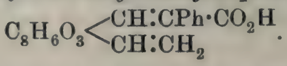
0·1690 gave 0·3278 $CO_2$ and 0·0829 $H_2O$. C=52·9; H=5·4.

0·1345 „ 0·0546 AgI. I=21·9.

$C_{24}H_{30}O_5NI,CH_4O$ requires C=52·6; H=5·9; I=22·1 per cent.

There can be no doubt that the substance contains one molecule of methyl alcohol of crystallisation.

### 2-*Methoxy*-3:4-*methylenedioxy*-6-*vinyl*-α-*phenylcinnamic Acid*,



$$C_8H_6O_3\left\langle\begin{matrix}CH{:}CPh\cdot CO_2H\\ CH{:}CH_2\end{matrix}\right.$$.

The methiodide (8 grams), just described, was converted into methochloride by heating with silver chloride (6 grams) in aqueous solution. After filtration the solution was treated with potassium hydroxide (8 c.c. of 40 per cent. aqueous solution), and boiled until the evolution of trimethylamine ceased. On cooling the liquid a sparingly soluble potassium salt separated, and this was purified by recrystallisation from water. The pure potassium salt was dissolved in water, and acidified with hydrochloric acid, when a colourless precipitate was obtained, which was collected, washed with water, and dried:

0·1240 gave 0·3188 $CO_2$ and 0·0595 $H_2O$. C=70·1; H=5·3.

$C_{19}H_{16}O_5$ requires C=70·4; H=4·9 per cent.

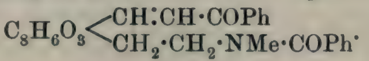
The acid could not be crystallised, but when prepared very carefully in the manner described above was found to melt at 144—146°. It is of interest that this doubly unsaturated substance only combines with two atoms of bromine:

0·9430 absorbed in chloroform solution 0·48 Br.

This weight of a substance, $C_{19}H_{16}O_5$ (absorbing two atoms of Br), would require 0·47 Br.

Clearly the vinyl group has been saturated, but, as in the case of benzoylanhydrocotarninephenylacetic acid (see p. 365), the second ethylenic linking is protected by the heavy groups which surround it. The dibromo-acid remaining in the chloroform could not be isolated in a pure condition.

### *Benzoylanhydrocotarnineacetophenone*,



$$C_8H_6O_3{<}\begin{array}{l}CH{:}CH{\cdot}COPh\\CH_2{\cdot}CH_2{\cdot}NMe{\cdot}COPh\end{array}\cdot$$

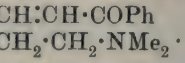
The condensation of cotarnine and acetophenone has been effected by Liebermann and Kropf (*Ber.*, 1904, **37**, 211), but the sodium carbonate, recommended by these authors as a condensing agent, is unnecessary, since under the following conditions an almost theoretical yield of pure substance may be obtained.

Cotarnine (31·6 grams) and acetophenone (16 grams) were dissolved in methyl alcohol (40 c.c.), and the solution allowed to remain at the room temperature for six hours. The introduction of a small crystal of the condensation product, or scratching of the walls of the vessel, now caused a plentiful crystallisation, and the product after collection weighed 43·5 grams. A further small quantity was recovered from the mother liquor. Kropf (*Ber.*, 1904, **37**, 2744) subjected this condensation product to the action of benzoyl chloride and aqueous potassium hydroxide, and obtained a benzoyl derivative, to which he ascribed the melting point 107—108°. In repeating this process we have obtained, although in poor yield, a compound melting at 131—132°, and this is undoubtedly anhydrobenzoylcotarnineacetophenone, since the same substance may also be obtained by the following method: Benzoylcotarnine (2·5 grams) and acetophenone (1·1 grams) were dissolved in ethyl alcohol (20 c.c.) mixed with aqueous potassium hydroxide (0·3 c.c. of 50 per cent.), and the solution gently heated on the steam-bath during twenty-four hours. The product separated on cooling, and was purified by crystallisation from methyl alcohol, or from a mixture of benzene and light petroleum:

0·1754 gave 0·4710 $CO_2$ and 0·0946 $H_2O$. C=73·2; H=5·9.
0·1616 „ 4·35 c.c. $N_2$ at 18° and 760 mm. N=3·1.
$C_{27}H_{25}O_5N$ requires C=73·1; H=5·6; N=3·2 per cent.

This substance crystallises in characteristic, greenish-yellow tufts of needles melting at 131—132°, and yields in sulphuric acid an intensely red solution. The process described above results in a very good yield of the substance, but the amount of potassium hydroxide cannot be varied very much. With less the condensation is too slow, whilst if more is employed a precipitate of potassium benzoate is produced. The identity of the substance with that obtained by the benzoylation of anhydrocotarnineacetophenone was proved by the fact that a mixture of the two substances melted sharply at 131—132°. It is interesting to note that benzoylcotarnine does not condense *per se* with ketones, etc., but is similar in its reactions to cotarnone and other aromatic aldehydes.

### *Phenyl* 2-*Methoxy*-3:4-*methylenedioxy*-6-β-*dimethylaminoethylstyryl Ketone*,



$$C_8H_6O_3<\begin{matrix}CH{:}CH\cdot COPh\\ CH_2\cdot CH_2\cdot NMe_2\end{matrix}.$$

The action of methyl iodide on anhydrocotarnineacetophenone was investigated by Kropf (*loc. cit.*), who states that the main product obtained when the reaction is conducted in methyl-alcoholic solution is a methyl methiodide of the base, whilst with an excess of the methyl iodide alone the hydriodide of methylanhydrocotarnineacetophenone is produced. We have confirmed the first part of this statement, but regard the production of a dimethyl iodide as another example of the opening of the hydrocotarnine ring, so that the action of methyl iodide on anhydrocotarnineacetophenone resembles that of the same reagent on anhydrocotarninenitromethane (Hope and Robinson, T., 1911, **99**, 2120). On the other hand, we believe that Kropf's methylanhydrocotarnineacetophenone hydriodide is in reality a normal methiodide of anhydrocotarnineacetophenone, and experimental evidence in favour of this view is given below. Although the nature of the products of the action of methyl iodide on the base varies according to the conditions of the reaction, this is not the case with methyl sulphate, and a straightforward methylation without secondary products was achieved.

### *Anhydrocotarnineacetophenone Methosulphate.*

Anhydrocotarnineacetophenone dissolved in warm benzene was treated with pure methyl sulphate (1·5 mol.), when in a short time the additive compound crystallised from the solution in theoretical amount. It was collected, washed with light petroleum, and crystallised from methyl alcohol. Large, colourless prisms were obtained, melting at 195—200° without decomposition.

The substance is readily soluble in hot methyl alcohol, sparingly so in the cold solvent.

When treated in aqueous solution with potassium iodide, anhydrocotarnineacetophenone methiodide is obtained. This substance crystallises from methyl alcohol in diamond-shaped prisms, and is identical in every way with the product of the action of methyl iodide on anhydrocotarnineacetophenone. It melts at 180° with very little decomposition. (Kropf, *loc. cit.*, gives 171° as the melting point of his methylanhydrocotarnineacetophenone hydriodide.)

The base figured at the head of this section (compare Kropf, *loc. cit.*) was prepared in the following manner: A solution of the above methosulphate (10 grams) in warm water (500 c.c.) was covered with an equal volume of light petroleum (b. p. 50—60°), and rendered strongly alkaline by means of potassium hydroxide. The colourless precipitate at first produced does not dissolve in the petroleum, and probably consists of the ammonium hydroxide, which, however, quickly decomposes, and yields a yellow substance which is completely extracted by the petroleum. The extract was dried with potassium carbonate, and after concentration deposited a mass of yellow, prismatic needles, melting after recrystallisation at 74—75°. (Found, C=71·4; H=6·6. Calc., C=71·4; H=6·5 per cent.)

Kropf (*loc. cit.*) assigned the melting point 78° to this substance, which he obtained by the action of alkali on anhydrocotarnineacetophenone methiodide.

*The Hydriodide.*—This derivative is of interest, since we have found by direct comparison that it is quite different from the methiodide of anhydrocotarnineacetophenone, which latter must, therefore, have a hydrocotarnine structure. It was obtained by the addition of potassium iodide to a solution of the above methyl base in dilute sulphuric acid. It crystallises from methyl alcohol, in which it is very readily soluble, in rectangular prisms containing solvent of crystallisation. This is lost at 100°, and the yellow powder then melts at about 156°. It differs from the isomeric methiodide markedly in combining both with water and methyl alcohol of crystallisation.

The *perchlorate* crystallises from methyl alcohol in pale yellow, slender needles, melting at 133—135°. It is very sparingly soluble in hot water.

The *picrate* is prepared by mixing hot acetone solutions of picric acid and the base. It crystallises from acetone in large, orange prisms, is sparingly soluble, and melts at 196°.

The *ferrichloride* prepared in the usual way crystallises from acetic acid in compact, reddish-brown prisms, melting at 176°.

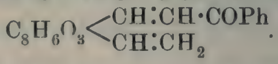
*The Methosulphate.*—This compound was prepared from its components exactly as in the case of anhydrocotarnineacetophenone methosulphate (see above). The product was crystallised from methyl alcohol, and obtained in yellow needles, which soften at 205°, and melt and decompose at 236°. Its solutions in water and methyl alcohol are intensely yellow:

0·1166 gave 0·0566 $BaSO_4$. S = 6·7.

$C_{23}H_{29}O_8NS$ requires S = 6·6 per cent.

*The Methiodide.*—The purest specimens of this derivative were obtained by the action of potassium iodide on the above methosulphate in aqueous solution. The product was crystallised from methyl alcohol, and obtained in pale yellow prisms melting at 238—239°. The same substance is produced by the direct addition of methyl iodide to the methyl base, and also by the action of methyl iodide on anhydrocotarnineacetophenone under the conditions described by Kropf (*loc. cit.*). Prolonged recrystallisation of these products raises their melting points to 238—239° (Kropf gives 226°).

### *Phenyl* 2-*Methoxy*-3:4-*methylenedioxy*-6-*vinylstyryl Ketone* (*Cotarnonideneacetophenone*),



$$C_8H_6O_3 \begin{cases} CH{:}CH{\cdot}COPh \\ CH{:}CH_2 \end{cases}.$$

The methiodide (5 grams) described at the end of the last section was dissolved in the least possible amount of hot water, and treated with silver chloride (4 grams) so as to obtain the more soluble methochloride. The filtered liquid was cooled to 50°, and mixed with 10 c.c. of *N*-sodium hydroxide solution, and allowed to remain during twenty-four hours. The yellow solution had a strong odour of acetophenone and trimethylamine, and after filtration was rapidly distilled, the flask being immersed in an oil-bath. The distillate contained trimethylamine (platinichloride, m. p. 238°) and acetophenone (piperonylidene derivative, m. p. 122°). The distillation was stopped when the liquid had reached one-third of its original volume, and the evaporation was continued on the steam-bath. The residue was treated with dilute hydrochloric acid, the solid separated and crystallised from methyl alcohol, and then again from ethyl alcohol. It was so obtained in pale yellow, prismatic crystals melting at 103°, this value being unaltered by admixture of the substance with an equal quantity of cotarnonideneacetophenone prepared as described below. The methyl-alcoholic mother liquor was diluted with an equal volume of water, the solution warmed with animal charcoal, cooled, filtered, and extracted with ether. The ethereal solution was dried, and evaporated nearly to dryness, when a small quantity of crystals melting at 78° was obtained. The substance was thus identified as cotarnone, and this was confirmed by the preparation of the condensation product with 2:4-dinitrotoluene, which melts at 163° (Hope and Robinson, T., 1911, **99**, 2131).

### *Synthesis of Cotarnonideneacetophenone.*

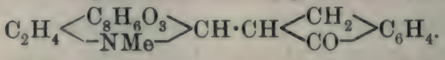
Cotarnone (3 grams) and acetophenone (3 grams) were dissolved in methyl alcohol (30 c.c.) and heated on the steam-bath for ten minutes with potassium hydroxide (6 c.c. of 30 per cent. aqueous solution). On cooling an oil separated, which became partly solid after scratching the sides of the containing vessel. The substance was collected, and thoroughly freed from oily impurities by contact with porous porcelain. It was then crystallised from ethyl alcohol, and obtained in pale yellow prisms melting at 103°:

0·1269 gave 0·3430 $CO_2$ and 0·0590 $H_2O$. $C=73·7$; $H=5·2$.
$C_{19}H_{16}O_4$ requires $C=74·0$; $H=5·2$ per cent.

The solution of the substance in concentrated sulphuric acid is red, and the addition of water produces a pale green precipitate.

*Cotarnonideneresacetophenone dimethyl ether* was obtained by the condensation of cotarnone with resacetophenone dimethyl ether by means of potassium hydroxide in alcoholic solution. It separates in yellow prisms from ethyl alcohol, in which it is sparingly soluble in the cold, and melts at 117°. The bright red solution of this unsaturated ketone in sulphuric acid is formed only momentarily, and quickly becomes orange owing to the production of the sulphate of a pyrrylium base. This was proved by the behaviour of the precipitate and solution obtained on pouring into water, for on the addition of hydrochloric acid a soluble oxonium salt was obtained, and this gave an orange-red platinichloride and picrate.

### *Anhydrocotarnine*-1-*hydrindone*,



$$\mathrm{C_2H_4}<\substack{\mathrm{C_8H_6O_3}\\ \mathrm{-NMe-}}>\mathrm{CH\cdot CH}<\substack{\mathrm{CH_2}\\ \mathrm{CO-}}>\mathrm{C_6H_4}.$$

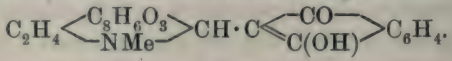
Cotarnine (10 grams) and 1-hydrindone (6 grams) were dissolved in methyl alcohol (20 c.c.), and the solution allowed to remain during a week. On scratching the walls of the containing vessel crystallisation was induced; the substance was then collected and crystallised from benzene and light petroleum, and then again from ethyl acetate, when it was obtained in colourless prisms melting at 126°:

0·1470 gave 0·3887 $CO_2$ and 0·0809 $H_2O$. C=72·1; H=6·1.

$C_{21}H_{21}O_4N$ requires C=71·8; H=6·0 per cent.

In properties the compound resembles the analogous anhydrocotarnineacetophenone, being rather more sparingly soluble in the usual solvents. Its salts are stable in aqueous solution, but the base is decomposed by boiling with acetic acid with formation of 1-hydrindone, which was recognised as its semicarbazone melting at 238°.

### *Anhydrocotarnine*-1:3-*diketohydrindene*,



$$\mathrm{C_2H_4}<\substack{\mathrm{C_8H_6O_3}\\ \mathrm{-NMe-}}>\mathrm{CH\cdot C}\lessdot\substack{\mathrm{-CO-}\\ \mathrm{C(OH)}}>\mathrm{C_6H_4}.$$

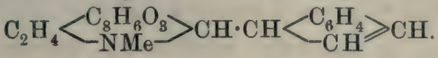
Diketohydrindene (1·9 grams) was ground with a solution of cotarnine (3·8 grams) in methyl alcohol (20 c.c.). The ketone dissolved in the liquid, forming a yellowish-brown solution, from which in a few seconds the new compound separated as a bright, canary-yellow precipitate, which under the microscope was seen to consist of aggregates of small needles. The substance was collected, washed with alcohol, and dried in a vacuum, after which it melted at 188° with vigorous decomposition:

0·1288 gave 0·3279 $CO_2$ and 0·0652 $H_2O$. C=69·4; H=5·6.

$C_{21}H_{19}O_5N$ requires C=69·0; H=5·2 per cent.

The compound is sparingly soluble in neutral organic solvents, and recrystallisation is not a profitable process. Its bright yellow colour might suggest that its constitution is analogous to that of benzylidenediketohydrindene, but against this may be cited the fact that the compound is soluble to an orange solution in cold dilute potassium hydroxide and in hot aqueous sodium carbonate. The yellow colour and solubility in alkalis are in agreement with the suggested enolic formula. A solution of the base in dilute acetic acid may be boiled without evident decomposition, and the same is true of its suspension and partial solution in aqueous sodium acetate. When, however, a little sodium acetate is added to a dilute acetic acid solution, then a crimson colour appears slowly in the cold, but rapidly on boiling. On cooling the colour almost disappears, and a pale yellow, crystalline substance separates from the liquid.

### *Anhydrocotarnineindene,*



$$C_2H_4<\substack{C_8H_6O_3 \\ NMe}>CH\cdot CH<\substack{C_6H_4 \\ CH}\geqslant CH.$$

Indene (7 grams) was mixed with cotarnine (14 grams) and methyl alcohol (30 c.c.), and the solution allowed to remain at the ordinary temperature during three days. Water (120 c.c.) and concentrated hydrochloric acid (30 c.c.) were then added, and the liquid boiled and filtered. The cooled solution deposited a quantity of a crystalline hydrochloride, which was recrystallised from hot dilute hydrochloric acid, in which it is remarkably sparingly soluble. The salt crystallises in short, slender needles, and has a beautiful, satiny appearance. It was decomposed with dilute ammonia, and the resulting almost colourless base twice crystallised from methyl alcohol. *Anhydrocotarnineindene* is readily soluble in most organic solvents, but sparingly so in cold methyl alcohol, from which it separates in prismatic needles melting at 136°:

0·1505 gave 0·4125 $CO_2$ and 0·0860 $H_2O$. C = 74·8; H = 6·3.

$C_{21}H_{21}O_3N$ requires C = 75·2; H = 6·3 per cent.

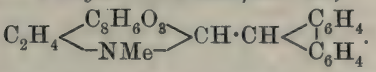
The salts of this base are for the most part sparingly soluble in water; the *sulphate* crystallises from hot dilute sulphuric acid in colourless needles with a satiny appearance.

*The Picrate.*—This derivative crystallises when alcoholic solutions of its components are mixed. It may be readily recrystallised from ethyl alcohol, in which it is rather sparingly soluble, and forms long, yellow needles, melting and decomposing at 170°:

0·1462 gave 12·4 c.c. $N_2$ at 13° and 760 mm. N = 10·1.

$C_{27}H_{24}O_{10}N_4$ requires N = 9·9 per cent.

### *Anhydrocotarninefluorene,*



$$C_2H_4<\substack{C_8H_6O_3 \\ NMe}>CH\cdot CH<\substack{C_6H_4 \\ | \\ C_6H_4}.$$

Fluorene (7 grams) was left in contact with a solution of cotarnine (10 grams) in methyl alcohol (50 c.c.). After twenty-four hours the liquid was heated until the fluorene had passed into solution, and this process was repeated thrice. Dilute hydrochloric acid was added, and the unchanged hydrocarbon removed by filtration, the acid solution being then basified with ammonia. The viscid precipitate was collected, dissolved in ether, the ethereal solution thoroughly dried, and evaporated nearly to dryness. The condensation product crystallised slowly from the solution, and was again crystallised from dry ether, and finally from ethyl alcohol. It was so obtained in colourless prisms, melting at 143° with very slight decomposition:

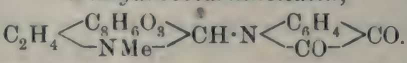
0·1512 gave 0·4303 $CO_2$ and 0·0815 $H_2O$. C=77·6; H=5·9.

$C_{25}H_{23}O_3N$ requires C=77·9; H=6·0 per cent.

The substance is sparingly soluble in neutral solvents, but dissolves readily in dilute hydrochloric acid, and the solution yields the usual sparingly soluble double salts with the appropriate reagents.

The *picrate* is readily obtained on mixing acetone solutions of the base and picric acid. It crystallises in canary-yellow prisms melting at 183°.

*Anhydrocotarnineisatin*,



$$C_2H_4<\substack{C_8H_6O_3\\ -NMe-}>CH\cdot N<\substack{C_6H_4\\ -CO-}>CO.$$

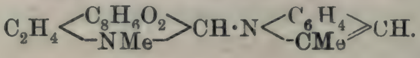
Methyl alcohol (25 c.c.) was poured on a mixture of cotarnine (7 grams) and isatin (4 grams). The solids passed into solution, but very quickly the condensation product separated in orange-red prisms. The substance may be recrystallised from acetone. It is sparingly soluble in alcohol, benzene, or ether, and melts at 146° with vigorous decomposition:

0·1343 gave 0·3213 $CO_2$ and 0·0617 $H_2O$. C=65·3; H=5·1.

$C_{29}H_{18}O_5N_2$ requires C=65·6; H=4·9 per cent.

This compound is a base, but it is decomposed in dilute acid solution, yielding a cotarnine salt and isatin. Cotarnine does not appear to condense with diphenylamine or carbazole.

*Anhydrocotarnine-α-methylindole*,



$$C_2H_4<\substack{C_8H_6O_2\\ -NMe-}>CH\cdot N<\substack{C_6H_4\\ -CMe-}>CH.$$

A solution of α-methylindole (7 grams) and cotarnine (12 grams) in methyl alcohol (25 c.c.) was allowed to remain overnight, when the whole of the condensation product was found to have separated as a hard, colourless mass, which when broken up resembled porcelain. The substance was dissolved in methyl ethyl ketone and the solution diluted with methyl alcohol, when the compound again crystallised as a hard mass, which was observed under the microscope to consist of prismatic crystals:

0·1350 gave 0·3572 $CO_2$ and 0·0783 $H_2O$. C=72·1; H=6·4.

$C_{21}H_{22}O_3N_2$ requires C=72·0; H=6·3 per cent.

The substance melts at 182° to a red liquid, and is sparingly soluble in most solvents. It dissolves unchanged in dilute hydrochloric acid to a colourless solution, which has no odour of α-methylindole. On boiling the liquid, decomposition with formation of α-methylindole and cotarnine slowly occurs, and the same reaction is complete and more rapid when the base is boiled with glacial acetic acid. The properties of this and of some other of the substances described above will be subjected to further investigation.

In conclusion, the authors desire to state that much of the expense of this investigation has been met by a grant from the Research Fund of the Chemical Society.

THE UNIVERSITY,
MANCHESTER.

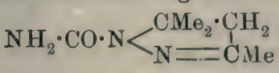
# XLV.—*Contributions to Our Knowledge of Semicarbazones. Part II. Semicarbazones of Mesityl Oxide.*

By FORSYTH JAMES WILSON and ISIDOR MORRIS HEILBRON.

IN a previous paper (T., 1912, **101**, 1482) the authors have shown that phenyl styryl ketone yields four stereoisomeric semicarbazones: two stable under ordinary conditions and two existing only in alkaline solutions.

In order to investigate the conditions of semicarbazone formation in the case of a simple aliphatic unsaturated ketone, mesityl oxide was selected. A semicarbazone of mesityl oxide was prepared by Scholtz (*Ber.*, 1896, **29**, 612), and further investigated by Harries and Kaiser (*Ber.*, 1899, **32**, 1338), who obtained it in a purer condition melting at 162—164°.

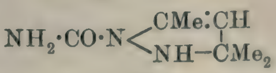
By distillation of this semicarbazone, Scholtz obtained a substance isomeric with it, but incapable of hydrolysis by acid. Harries and Kaiser showed that this isomeric substance melting at 129° was not a stereoisomeric semicarbazone, but a basic compound yielding a picrate, and evidently structurally different from the semicarbazone. These authors, on account of the great stability of this substance, considered that it possessed a cyclic constitution, and proposed the following two formulæ:



$$NH_2\cdot CO\cdot N<\begin{matrix}CMe_2\cdot CH_2\\ | \\ N{=\!=}CMe\end{matrix}$$

(I.)

or

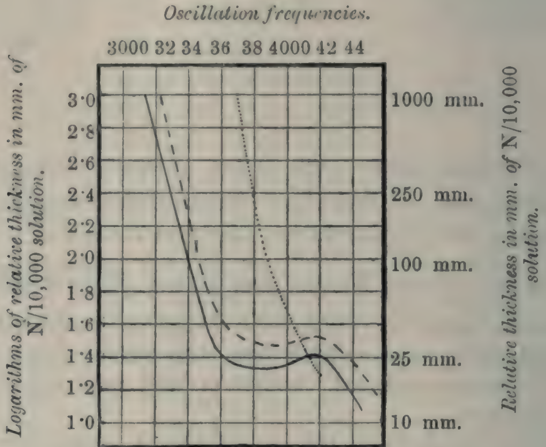


$$NH_2\cdot CO\cdot N<\begin{matrix}CMe{:}CH\\ | \\ NH-CMe_2\end{matrix}$$

(II.)

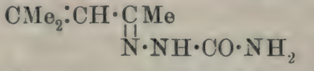
These formulæ were discussed later by Rupe and Kessler (*Ber.*, 1909, **42**, 4503), who proved definitely that formula I was inadmissible, whilst formula II, although probably correct, could not be confirmed.

As, however, two stereoisomeric oximes of mesityl oxide have been obtained, it seemed to the authors that two stereoisomeric semicarbazones should be capable of existence. It was found that these expectations could be realised by exposure of the ordinary semicarbazone ($\alpha$-form) to ultraviolet light, when it was partly converted into a stereoisomeride ($\beta$-form) melting at 133—134°. Conversely, the $\beta$-isomeride on exposure to ultraviolet light was partly converted into the $\alpha$-form. That this new $\beta$-isomeride is a true semicarbazone is shown by the ease with which it is hydrolysed by dilute acid with regeneration of mesityl oxide.



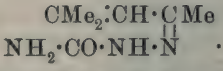
*α-Semicarbazone in alcohol* (full curve).
*β-* ,, ,, ,, (dash curve).
*Cyclic compound* ,, ,, (dot curve).

According to theory only two stereoisomerides are possible, as represented by the following formulæ:



$$\begin{array}{l}\mathrm{CMe_2{:}CH{\cdot}CMe}\\ \qquad\qquad\quad \Vert\\ \qquad\qquad\quad \mathrm{N{\cdot}NH{\cdot}CO{\cdot}NH_2}\end{array}$$

and



$$\begin{array}{r}\mathrm{CMe_2{:}CH{\cdot}CMe}\\ \Vert\quad\ \ \\ \mathrm{NH_2{\cdot}CO{\cdot}NH{\cdot}N}\quad\ \ \end{array}.$$

The absorption spectra of the $\alpha$- and $\beta$-forms in alcoholic solution are indicated in the figure, the full curve representing the $\alpha$-form, the dash curve the $\beta$-isomeride. Both forms show a shallow band with head at 3900, and are practically identical, as is to be expected from a case of purely nitrogen stereoisomerism.

In the case of the semicarbazones of phenyl styryl ketone (*loc. cit.*), where four stereoisomerides were possible, the effect of light on the solid substances or of alkali on their solutions was to produce yellow stereoisomerides. In the present case neither semicarbazone was phototropic, nor had alkali any effect on the absorption spectra. Apparently phototropic and thermotropic properties and the shifting to the red of the absorption spectra by alkali require, in the case of semicarbazones, both carbon and nitrogen stereoisomerism. As further proof of this, we have found that with the semicarbazones of cinnamaldehyde and of styryl methyl ketone, where both carbon and nitrogen stereoisomerism are possible, phototropic and thermotropic properties are developed, and also alkali shifts the absorption band towards the red end of the spectrum, whilst semicarbazones of saturated ketones show none of these properties. We hope shortly to publish these results in detail.

The β-modification was distilled in the hope of obtaining a cyclic compound differing from that obtained by Scholtz. The compound obtained, however, was in every way identical with the substance produced by the distillation of the α-form; this can be explained by the fact that we have found that the β-form is unstable, for it was noticed that from specimens of the β-form which had been kept for some time a rise in melting point had occurred. It was found that if the β-form was kept above its melting point for a few minutes it was converted with some decomposition into the α-form. That the cyclic compound melting at 129° is entirely different in constitution from either semicarbazone, is borne out by its absorption spectrum (dotted curve), as shown in the figure.

## EXPERIMENTAL.

The mesityl oxide semicarbazone was prepared from mesityl oxide according to the methods of Scholtz (*loc. cit.*) and Rupe and Kessler (*loc. cit.*). The yield of semicarbazone by either method was very variable, even under apparently identical conditions. In some cases, indeed, no semicarbazone at all was produced.

The pure semicarbazone was found to melt sharply at 164°.

*β-Modification.*—This was obtained from the α-isomeride by exposing it in chloroform solution to a quartz mercury lamp for thirty hours (distance from lamp, 10 cm.). The solution gradually became red and turbid, and was finally separated by filtration from a small amount of an amorphous, red substance. The chloroform was then distilled off, and the residue fractionally crystallised from benzene. The first crop of crystals consisted chiefly of unchanged α-semicarbazone, the more soluble β-modification crystallising out from the mother liquors on concentration. The yield of this isomeride was about 30 per cent., an equilibrium evidently existing between the two forms, for exposure to the ultraviolet light for longer periods than thirty hours did not increase the yield of this new form.

After a further recrystallisation from benzene the β-semicarbazone was obtained in small, white crystals, melting at 133—134°, readily soluble in alcohol or hot water, but less so in benzene:

0·1744 gave 40·2 c.c. $N_2$ at 15° and 758 mm. N = 27·13.
0·102, in 14·5 of chloroform, gave E = 0·153°. M.W. = 168.
0·201, „ 14·5 „ „ „ E = 0·320°. M.W. = 166.
$C_7H_{13}ON_3$ requires N = 27·09 per cent. M.W. = 155.

On warming this β-semicarbazone with dilute hydrochloric acid, hydrolysis took place almost immediately with evolution of the readily volatile mesityl oxide vapours.

These results indicate that this β-isomeride is a true semicarbazone, and stereoisomeric with the α-form.

*Conversion of the β- into the α-Modification.*—As it was found previously by us that the semicarbazones of phenyl styryl ketone on exposure to ultraviolet light were interconvertible, it was expected that the same would hold for the α- and β-mesityl oxide semicarbazones. That this assumption was correct was proved by exposing the β-semicarbazone in chloroform solution to ultraviolet light for thirty hours. The solution was then treated as already described, the product on fractional crystallisation from benzene yielding approximately 60 per cent. of the α-isomeride.

The conversion of the β- into the α-stereoisomeride could also be brought about by keeping the β-semicarbazone at a temperature above its melting point (150—160°) for some minutes. The fusion was allowed to cool, and, on crystallisation of the dark-coloured solid residue from benzene, a considerable quantity of the α-semicarbazone was obtained.

*Preparation of the Isomeric Cyclic Compound melting at* 129°.—The substance was prepared by distillation of the α-form as described by Scholtz, and purified by crystallisation from carbon disulphide. On repeating the experiment with the β-semicarbazone, the reaction proceeded in a similar manner, but the yield of the cyclic compound in this case was poor, considerable decomposition taking place, probably during the primary transformation of the β- into the α-isomeride. That the products as obtained from either form were identical was shown by a mixed melting-point determination.

In conclusion, we desire to express our thanks to the Carnegie Trust for the Universities of Scotland for a grant which has defrayed the expenses of this investigation.

CHEMISTRY DEPARTMENT,
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# XLVI.—*The Chemical Nature of Some Radioactive Disintegration Products.*

By **Alexander Fleck**, B.Sc.

Many of the radio-elements have been shown, after close examination, to resemble other elements, and to be non-separable from them by chemical processes; thus the impossibility of separating radio-lead (radium-*D*) from lead, mesothorium-1 and thorium-*X* from radium, ionium and radio-thorium from thorium is well known (Soddy, "Chemistry of the Radio-elements"). The chemistry of the best known disintegration products is summed up by saying that they are identical with such elements as lead in the case of radium-*D*, or as radium in the case of mesothorium-1. Other such resemblances no doubt exist, and in the present paper a systematic investigation has been made of all the radio-elements of period sufficiently long for chemical examination, in the course of which it has been shown that many of the radio-elements known to resemble other elements, either radio-active or inactive, are, in fact, non-separable from them, and several new cases of the same kind have been discovered. The work detailed in this paper increases the number of disintegration products the chemistry of which can be referred to the chemistry of ordinary non-radio-active elements.

## *Uranium*-X.

One of the methods used by Sir W. Crookes (*Proc. Roy. Soc.*, 1900, **66**, 409) when he discovered uranium-*X* was to dissolve uranyl nitrate containing a small quantity of an iron salt in excess of dilute ammonium carbonate solution, when most of the iron remained undissolved, and this contained the $\beta$-activity due to uranium-*X*. Other methods of separating this substance are known, but until recently these methods have been quite empirical. Among such methods are: (1) Shaking uranyl nitrate, crystallised from water, with ether. The uranyl nitrate dissolves mainly in the ether, whilst the aqueous layer from the water of crystallisation contains the uranium-*X*. (2) Precipitating barium sulphate in a solution of uranyl nitrate. The uranium-*X* is adsorbed by barium sulphate and can be collected with it.

In 1909 Soddy (*Phil. Mag.*, 1909, [vi], **18**, 858) collected uranium-*X* from 50 kilos. of uranyl nitrate in a highly concentrated form. The exact nature of the impurities which contained the uranium-*X* was not determined, but it was found possible to dissolve them in concentrated ammonium carbonate, and from the solution so obtained they could be fractionally precipitated by boiling. In some cases the uranium-*X* was precipitated almost entirely in the last minute fraction, and in other cases in one of the intermediate fractions. The uranium-*X* did not seem to follow any general law, but the separation was, as a rule, sharp.

In the same year Ritzel (*Zeitsch. physikal. Chem.*, 1909, **67**, 725) found that if charcoal is shaken with a solution of uranium-*X* the charcoal adsorbs the uranium-*X*. If, however, a trace of thorium sulphate is present the uranium-*X* is not adsorbed. Later Marckwald (*Ber.*, 1910, **43**, 3421) and Keetman (*Jahrb. Radioaktiv. Elektronik.*, 1909, **6**, 265) stated that they had found that they could not separate uranium-*X* from thorium, but they gave no details of their attempts. If uranium-*X* and thorium are non-separable, the general explanation of Ritzel's experiment follows at once (Soddy, T., 1911, **99**, 72).

The question of the non-separability of uranium-*X* and thorium by chemical methods was subjected to as rigorous an examination as possible. In doing this one of two methods was used: either a mixture of thorium, another element, and uranium-*X* was made, and the second element separated as completely as possible from the thorium, after which the β-activities of the two portions were measured, and the relative amounts of uranium-*X* present in each thus determined; or a mixture of thorium and uranium-*X* was made, and the thorium separated into fractions by some systematic method, after which the β-radioactivity of the fractions was measured in the electroscope, and then their content of thorium estimated in the usual way gravimetrically, by precipitating an acid solution with oxalic acid, igniting the precipitate, and weighing as thorium oxide. In this way the activity per gram of thorium oxide was obtained. The quantity of uranium-*X* was always measured by the β-radiation from a thin layer in a standard position with an electroscope which had an aluminium base 0·1 mm. thick.

Uranium-*X* was separated from uranium with iron, dissolved in dilute acid, and added to a boiling solution of sodium thiosulphate. The sulphur which is thereby precipitated does or does not contain the uranium-*X*, according as the solution is weakly or strongly acid. Thorium behaves in exactly the same manner. If a mixture of cerium, thorium, and uranium-*X* was made it was observed that the thorium, whether separated by sodium thiosulphate, hydrogen peroxide, or potassium azoimide, always contained the uranium-*X*. In a similar manner thorium, separated from zirconium—the mixture containing uranium-*X*—by dissolving both oxalates in excess of ammonium oxalate and then strongly re-acidifying the solution. contains all the β-activity.

The residues obtained by Soddy (*Phil. Mag.*, *loc. cit.*), from which uranium-$X$ had been separated, ought on this hypothesis to be free from thorium, which was found to be the case. When uranium-$X$ was mixed with them and the mixture fractionated by the ammonium carbonate method, it behaved indefinitely, but when thorium was added its separation with that element was sharp.

It is perhaps worth mentioning that a convenient method for redissolving ignited thorium oxide is to fuse it with sodium peroxide. More than 95 per cent. of thorium oxide was dissolved in one operation, and no appreciable quantity of uranium-$X$ remained undissolved.

Becquerel's original method of separating uranium-$X$ was by adsorption by barium sulphate. If uranium-$X$ and thorium are identical it is to be expected that the adsorption will be inhibited when the latter element is present. Barium sulphate precipitated in a uranium-$X$ solution which contained no thorium carried down 98 per cent. of it, and if this active barium sulphate is boiled with acid no uranium-$X$ passes into solution. A solution of barium, thorium, and uranium-$X$ was treated with sulphuric acid, and the barium sulphate had an activity of one-third of that of the thorium remaining in solution. The filtrate contained thorium and uranium-$X$, the latter giving a $\beta$-activity of 800·9 d.p.m.* per gram of thorium oxide. When the barium sulphate containing one-third of the uranium-$X$ was boiled with nitric acid, the barium sulphate became inactive, and the filtrate contained thorium, which gave an activity due to uranium-$X$ of 778·6 d.p.m. per gram of thorium oxide. The essential difference to be noted is this: if no thorium is present uranium-$X$ cannot be dissolved by boiling with acids when once it has been adsorbed by barium sulphate, but if thorium is present the barium sulphate carried down with it some thorium which can be redissolved by acids, and the concentration of the uranium-$X$ in the two portions of the thorium is constant. The presence of zirconium in a barium and uranium-$X$ solution has no effect whatever on the adsorption by barium sulphate. The presence, however, of cerium inhibits the complete adsorption of uranium-$X$ by barium sulphate, only two-thirds of the uranium-$X$ being adsorbed, but there is this essential difference from the case of thorium, that the uranium-$X$ contained in the precipitated sulphate cannot be redissolved by acids from it.

Boltwood (*Amer. J. Sci.*, 1908, [iv], **25**, 269) and others have used the following method of separating uranium and thorium; a mixture of the nitrates is evaporated to dryness at 110°, and then shaken with anhydrous ether. The uranium is stated to pass into solution, whilst the thorium remains undissolved. If this were so, it would be in complete accordance with the observed facts about the completeness of the separation of uranium-*X* from uranium by the ether method already mentioned. This separation of uranium and thorium has, however, been called into question, and has been the subject of some discussion (Soddy and Pirret, *Phil. Mag.*, 1910, [vi], **20**, 345; Mlle. E. Gleditsch, *Le Radium*, 1911, **8**, 256). The distribution ratio of uranium and thorium in ether, both anhydrous and containing various quantities of water, has been the subject of a detailed examination, and it has been found that the separation is only complete when small quantities of thorium are present; thus with less than 10 per cent. of thorium nitrate present, no thorium could be detected in the ethereal solution when the mixed nitrates were shaken with one volume of water and ten volumes of ether. Under the conditions of the ether-extraction process for uranium-*X* there is a relatively large quantity of ether compared with the quantity of water, and a very great weight of uranium compared with the weight of impurities present. Under these conditions no thorium would be dissolved by the ether, and it is known that no uranium-*X* is dissolved in it. From the solution of a mixture of thorium and uranium nitrates, 50 per cent. of each, it is possible to extract both thorium and uranium-*X* in the ethereal layer; thus, three successive extractions gave extracts with $\beta$-radioactivity corresponding with 10·94, 6·81, and 2·50 d.p.m. respectively, and the concentration of the uranium-*X* extracted by ether was represented by 129·7 d.p.m. per gram of thorium oxide, whilst that of the uranium-*X* remaining undissolved was 126·9 d.p.m. per gram of thorium oxide.

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* This refers to divisions per minute in arbitrary units.

A quantity of uranium-*X* containing iron was dissolved, and about 3 grams of thorium nitrate were added to the solution, which was then treated with excess of ammonium carbonate until the precipitated carbonate was redissolved. This solution was then boiled for a short time, the precipitate collected, and the boiling continued. In this way ten precipitates were formed as follows:

| No. of precipitate. | Activity. | Weight of ignited thorium oxalate. Gram. | Activity per gram of ignited oxalate. |
|---|---|---|---|
| 1 | 2·35 | 0·0380 | 61·95 |
| 2 | 8·98 | 0·1711 | 52·49 |
| 3 | 1·358 | 0·0225 | 60·36 |
| 4 | 4·056 | 0·0643 | 63·08 |
| 5 | 9·58 | 0·1499 | 63·90 |
| 6 | 14·02 | 0·2214 | 63·31 |
| 7 | 18·85 | 0·3026 | 62·30 |
| 8 | 30·97 | 0·4967 | 62·16 |
| 9 | 30·80 | 0·5221 | 59·0 |
| 10 | 3·977 | 0·0701 | 56·90 |

It is evident that no alteration in the concentration of uranium-$X$ and thorium has taken place. Another series of fractional precipitations was made, in which the concentration of uranium-$X$ in thorium was more than ten times as great as in the above series, but again it was proved that uranium-$X$ remains uniformly distributed throughout the thorium.

Experiments were now made with fractional crystallisation. Thorium acetate containing uranium-$X$ was dissolved in acetic acid, and the excess of acid slowly evaporated. The first crystals that appeared were removed, and the evaporation continued. In this way three fractions were obtained, which had activities of 169·2, 160·3, and 171·3 d.p.m. per gram of thorium oxide respectively.

Uranium-$X$ is one of the disintegration products that has never been volatilised. One of the methods of dissolving thorium oxide is to volatilise it in a stream of chlorine, when the anhydrous chloride collects in the cooler portions of the furnace. Thorium oxide containing uranium-$X$ was treated in this way, and the product divided itself into three parts: (1) thorium, which collected in the trap outside the furnace, (2) thorium collected in the cooler parts, and (3) thorium which remained unvolatilised. It was found that in none of these portions did the activity per gram of thorium oxide vary more than 4 per cent. from the mean.

Within the errors of experiment in none of these methods has any separation of uranium-$X$ from thorium been effected, although there is no known substance outside the radio-elements which would have remained with thorium through these varied chemical processes.

### *Radio-actinium.*

The usual method employed in the separation of radio-actinium (Hahn, *Ber.*, 1906, **39**, 1605; *Physikal. Zeitsch.*, 1906, **7**, 855) is to precipitate it with sulphur by adding an actinium solution to a boiling solution of sodium thiosulphate, but Hahn has shown that its separation is very uncertain.

Stromholm and Svedberg (*Zeitsch. anorg. Chem.*, 1909, **61**, 338; **63**, 197) have shown that radio-actinium is isomorphous with thorium, and that thorium-$X$ and actinium-$X$ are isomorphous with barium. This does not necessarily mean that thorium and radio-actinium are non-separable elements because radium and barium are isomorphous, yet these two elements can be separated. From analogy to the thorium and the actinium series it is to be expected that radio-actinium will be identical with radio-thorium, and hence with thorium. If this is so, Hahn's thiosulphate method should become sharp and definite in the presence of the smallest quantity of thorium.

The only β-ray substance in the actinium series is actinium-*D*, but the quantity of any of the long-lived substances, actinium, radio-actinium, or actinium-*X*, may be determined by β-ray measurements; thus, if we start with actinium-*X* free from other products the activity due to actinium-*D* rises to a maximum in two hours, and then falls with a period characteristic of actinium-*X*. In the case of a pure preparation of radio-actinium the activity will rise very much more slowly owing to the time required for the production of the intermediate actinium-*X*, and after reaching a maximum should decay to zero. If $\theta$ is the time required to reach a maximum value, then:

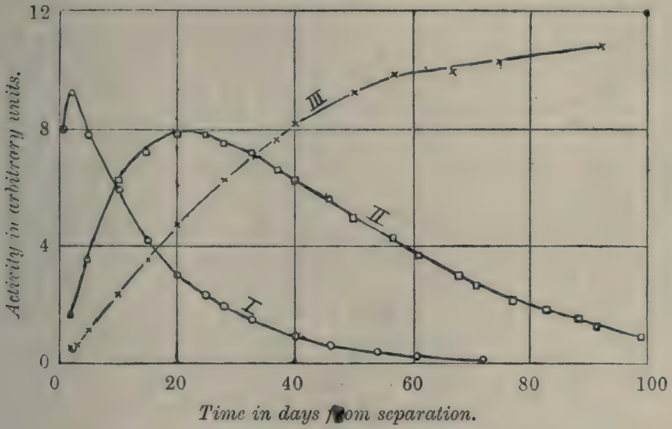
$$\theta = \log_e \lambda_2/\lambda_1 \Big/ (\lambda_2 - \lambda_1),$$

where $\lambda_1$ is the radioactive constant of radio-actinium, and $\lambda_2$ is the radioactive constant of actinium-*X*. Taking $\lambda_1^{-1} = 28{\cdot}1$ days, and $\lambda_2^{-1} = 15$ days, $\theta$ is calculated to be 20·23 days. From the form of the curves obtained in the various cases the initial purity of the preparation can be deduced quite easily.

About 0·1—0·2 gram of an actinium preparation containing lanthanum was dissolved in acid, and 20 milligrams of thorium nitrate were added. The solution was then rendered alkaline, and the precipitated actinium and thorium hydroxides were collected. The filtrate contained actinium-*X*, which was evaporated to dryness and ignited. The precipitated actinium and thorium hydroxides were redissolved in a slightly acid solution, and added to a boiling solution of sodium thiosulphate. A precipitate of sulphur is formed, and with it the thorium is precipitated as thorium hydroxide. The filtrate from this precipitate was evaporated to dryness and ignited. In this way three preparations were obtained: (1) the evaporated and ignited filtrate from the ammonia precipitation of actinium and thorium hydroxides, (2) the dried and ignited precipitate obtained by sodium thiosulphate, and (3) the evaporated and ignited filtrate from that precipitate. The second preparation will contain the thorium, and its activity should, if it contains radio-actinium, be initially zero, and then rise to a maximum in about twenty days, and finally decay again to zero. The third preparation should contain actinium free from either radio-actinium or actinium-*X*. Its β-activity should also be, initially, zero, but it should rise continually for a number of months. The three preparations were found to behave in the manner indicated (see Fig. 1). The separation of thorium from actinium was also effected with hydrogen peroxide and potassium azoimide, and in each case the β-activity of the precipitated thorium was initially very small, but rose to a maximum in about twenty days, and then decayed to zero, with a half period of from twenty-five to thirty days.

All the available quantity of actinium was taken, and the radio-actinium separated with a small quantity of thorium by sodium thiosulphate. More thorium was added to this preparation, so that the total quantity of thorium oxide present was about 0·2 gram. The whole was dissolved in concentrated ammonium carbonate solution, and then fractionally precipitated by boiling. The activity, measured when it had reached its maximum, per gram of thorium oxide is seen not to vary from a constant value beyond the limits of experimental error.

FIG. 1.



Curve I: *Activity of ammonia filtrate—Actinium-X.*
,, II: *Activity of thiosulphate precipitate—Radio-actinium.*
,, III: *Activity of thiosulphate filtrate—Actinium.*

| No. of precipitate. | Activity. | Weight of thorium oxide. Gram. | Activity per gram of thorium oxide. |
|---|---|---|---|
| 1 | 1·512 | 0·0118 | 12·81 |
| 2 | 1·614 | 0·0136 | 11·86 |
| 3 | 2·258 | 0·0184 | 12·25 |
| 4 | 3·398 | 0·0276 | 12·30 |
| 5 | 4·565 | 0·0383 | 11·92 |
| 6 | 4·748 | 0·0412 | 11·53 |
| 7 | 4·496 | 0·0393 | 11·84 |
| 8 | 0·596 | 0·0049 | 12·17 |

It has therefore been proved that thorium and radio-actinium are alike in chemical properties so far as they have been examined, and that in place of the separation of radio-actinium from actinium being indefinite, it is effected almost perfectly if a small quantity of thorium is added to the actinium and the former separated from the latter.

### *Mesothorium*-2.

Hahn (*Physikal. Zeitsch.*, 1908, **9**, 246), who discovered this substance, recommends for its separation from mesothorium-1 the use of zirconium. This element is added to a mesothorium solution and precipitated with ammonia, when it carries down the mesothorium-2 with it. In this separation any radiothorium which is present is precipitated with the mesothorium-2.

It is easily shown that mesothorium-2 is not precipitated by hydrogen sulphide, and that therefore it must belong to the third group. It seemed at first that it might be similar to thorium, but it was observed that when thorium is precipitated with potassium azoimide or hydrogen peroxide, mesothorium-2 remains in solution. By dissolving iron, uranium, etc., with mesothorium-2 in ammonium carbonate it was found that it could be concentrated in the more insoluble fractions, and that it was unlike any of the common elements of the third group. The fact that its oxalate was very soluble suggested that it might be similar to actinium. This was tested as follows: If we start with a mixture of mesothorium-2 and actinium free from radio-actinium and subsequent products, the initial activity, if $\beta$-rays are measured, will be entirely due to mesothorium-2, which will decay almost completely to zero in two days, in which time exceedingly little actinium-*D* will have grown from actinium. In the course of three or four months actinium-*D* will reach a maximum amount, owing to the radio-actinium and actinium-*X* attaining equilibrium. Therefore, by taking decay curves during the first two days, the relative amount of mesothorium-2 can be found, and, finally, by measuring the activity after equilibrium has been reached the relative amount of actinium present can be ascertained.

Mesothorium-2 was separated from a mesothorium preparation, free from radiothorium, by means of zirconium, and added to a quantity of actinium which had been freed by sodium thiosulphate from radio-actinium (see p. 386). The whole was dissolved in ammonium carbonate and reprecipitated by boiling, and thus divided into several fractions, care being taken that the first fractions were very small. For some time the quantity of actinium-*D* in the fractions was proportional to the quantity of mesothorium-2 that had initially been present, but gradually the quantity of actinium-*D* relative to mesothorium-2 became relatively smaller in the latter fractions, but finally that quantity has again increased until now it is again almost proportional to the quantity of mesothorium originally present.

| No. of precipitate. | Activity initially due to mesothorium-2. | Activity due to actinium-*D* (after 2½ months). | $\frac{\text{Activity of actinium-}D}{\text{Activity of mesothorium-2}}$. |
|---|---|---|---|
| 2 | 6·13 | 8·83 | 1·44 |
| 3 | 25·01 | 35·31 | 1·41 |
| 4 | 7·45 | 9·66 | 1·28 |

Precipitates number 1, 5, 6, and 7 were inactive.

Since the quantity of actinium-*D* is finally proportional to the quantity of actinium present, it is evident that mesothorium-2 has divided itself in the same proportion as actinium. The explanation of the lack of proportionality in the earlier stages of the experiment is that the separation of actinium from thorium is not complete by one precipitation with sodium thiosulphate, and, since it has been shown that radio-actinium is identical with thorium, some radio-actinium remains with the actinium. The solubility of thorium in ammonium carbonate solution is different from that of actinium, so that radio-actinium will not be equally distributed with the actinium, and consequently there will be in the earlier stages of the experiment more actinium-*D* where radio-actinium has accumulated. It is therefore necessary if a true measure of the quantity of actinium present is required to wait until equilibrium is reached.

Another experiment was made in which actinium free from radio-actinium and actinium-*X* was dissolved in strongly acid solution along with zirconium containing mesothorium-2. Oxalic acid was added, and the solution gradually neutralised, so that the oxalates were fractionally precipitated. The result at the present time is:

| No. of precipitate. | Activity initially due to mesothorium-2. | Activity due to actinium-*D* (after 2 months). | $\frac{\text{Activity of actinium-}D}{\text{Activity of mesothorium-2}}$. |
|---|---|---|---|
| 2 | 9·1 | 3·74 | 0·41 |
| 3 | 35·0 | 15·11 | 0·432 |
| 5 | 61·5 | 24·96 | 0·405 |
| 6 | 5·7 | 1·915 | 0·375 |
| 7 | 26·75 | 10·16 | 0·38 |
| 8 | 12·75 | 5·43 | 0·4255 |

It is to be expected that, as in the preceding experiment, the numbers in the last column will become more nearly equal as complete equilibrium is reached.

Mr. Cranston in this laboratory, who is using the method described for the separation of radiothorium from mesothorium-2, has obtained further evidence in favour of the view here taken that actinium and mesothorium-2 are chemically identical.

### *Chemistry of the Active Deposits.*

Very little is known about the chemistry of the "active deposit group," apart from their relative volatilities in air and other gases (A. S. Russell, *Phil. Mag.*, 1912, [vi], **24**, 134), but, on the other hand, considerable progress is being made on the electrochemical side. Evidence of this is seen in von Lerch's rule, that each succeeding substance is electrochemically "nobler" than the last, and in von Hevesy's recent paper (*Phil. Mag.*, 1912, [vi], **23**, 628) on their "electrochemistry." Although so little is known there seems to be a fairly general belief that they are allied to the noble metals.

Thorium-*B*, radium-*B*, and actinium-*B* give only a feebly penetrating ($\beta$)-radiation, but each gives a *C*-product which gives $\alpha$-rays. If, therefore, we start with the *B*-member in a pure condition its activity will be initially zero, but will rise to a maximum, and then, since in all cases the *B*-member has a longer period than the *C*-member, the activity will decay to zero with the period of the former. If $\alpha$-rays are measured, this maximum will be reached in 3·54 hours in the case of thorium-*B*, in 32·78 minutes in the case of radium-*B*, and in 9·29 minutes in the case of actinium-*B*, assuming the usual periods in all cases. If $\beta$-rays are measured,* the curves will be substantially of the same form as the $\alpha$-ray curves, except in the case of actinium, when the maximum for the $\beta$-rays will not be reached until a relatively greater time has elapsed, as in this case the *D*-member is longer lived than the *C*-member. If we start with the *C*-member initially pure, then the activity will decay from the beginning with a period of average life of 79, 28·1, 3·10 minutes, according as the substance is thorium-*C*, radium-*C*, or actinium-*C*.

### *Thorium*-B *and Thorium*-C.

It was observed that when a solution of a small quantity of lead was added to a solution in which the active deposit group of the thorium series was in radioactive equilibrium, and the lead precipitated completely as sulphide, the precipitate contained thorium-*B* and -*C* in equilibrium amount. If the solution was distinctly acid, so that the lead was not completely precipitated, there was excess of thorium-*C* in the quantity of sulphide obtained. If in addition to lead the solution contained tin or other metal the sulphide of which was soluble in ammonium sulphide, then, when that sulphide was removed by this reagent, no activity was found in the solution so obtained. This shows that neither thorium-*B* nor -*C* are allied to the noble metals as hitherto supposed. If a solution of lead and copper is precipitated with sodium carbonate and the precipitate digested with potassium cyanide solution, then the copper and any other second group metal present, with the exception of lead and bismuth, will be dissolved as a complex cyanide. In these circumstances, and in the presence of thorium-*B* and -*C*, it was found that no activity was contained in the potassium cyanide solution. This shows that both thorium-*B* and -*C* are similar to lead or bismuth.

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* This statement is not strictly true, because radium-*B* gives a small proportion of $\beta$-rays (compare Fajans and Makower, *Phil. Mag.*, 1912, [vi], 23, 293).

A solution of thorium-*B* and -*C* was treated with sulphuric acid and alcohol. The precipitated sulphate was removed, and hydrogen sulphide added to the filtrate to precipitate the bismuth. The activity of the lead sulphate was found to be, at the time of the first measurement, less than one-half of the value that it reached in three and a-half hours from the time of precipitation, and by producing the curves backwards from the time of the first reading until the moment of precipitation it was seen that the value then could not be more than from 8 to 12 per cent. of its maximum value. It is shown, therefore, that lead sulphate contains initially practically no thorium-*C*. On the other hand, the bismuth precipitated as sulphide gave an activity which decayed to half value in seventy-two minutes, and was therefore mainly due to thorium-*C*.

The separation of lead and bismuth containing thorium-*B* and -*C* in solution was effected in the following ways, and the activity of each precipitate measured:

(1) Lead precipitated as lead sulphate, bismuth as bismuth sulphide.

(2) Lead precipitated as lead sulphate, bismuth as bismuth hydroxide.

(3) Lead precipitated as lead chloride.

(4) Bismuth precipitated as bismuth oxychloride, lead as lead sulphide.

(5) Bismuth precipitated with *m*-nitrobenzoic acid, lead as lead hydroxide.

(6) Bismuth precipitated with alcohol.

In each of these cases it was found that the activity of the lead compound rose to a maximum, and then fell to half value in eleven hours, whilst the activity of the bismuth precipitate fell to half value with a period slightly longer than the usual value of thorium-*C*, as a rule about seventy-four to seventy-six minutes. The separation of the two metals was also effected electrolytically by depositing metallic bismuth on the cathode, and lead peroxide on the anode from an acid solution. The activity of the cathode deposit fell normally with the period of thorium-*C*, but the activity of the anode deposit rose only slightly or not at all before falling with the period of thorium-*B*. On analysis it was found that the lead peroxide contained considerable quantities of bismuth, and that, therefore, it was not possible to deposit lead and bismuth simultaneously in a pure condition.

The reaction mentioned above (No. 5) of separating bismuth by the use of *m*-nitrobenzoic acid is especially interesting. It was suggested by the work of Schlundt and Moore (*J. Physical Chem.*, 1905, **9**, 682), who found that thorium-*B* and thorium-*X* remained in solution, whilst thorium and the other products were precipitated by this reagent. Since it appears that thorium-*B* behaves as lead in all the reactions that have been tried, it was of interest to see if the converse is true, if lead will behave as thorium-*B* and will remain in solution, whilst bismuth, if it behaves as thorium-*C*, will be precipitated. This was tested and found to be the case, and a separation of these two metals could be made by this means. The precipitation of bismuth, either by *m*-nitrobenzoic acid or by alcohol, does not seem to be generally known, and it is intended to continue the examination of these two reactions to see if they are capable of application to analytical work.

Experiments were then made in the systematic fractionation of lead in a solution containing thorium-*B* to see if any difference of concentration of thorium-*B* in the various fractions could be noticed. Lead was fractionally precipitated by adding successive small quantities of sulphuric acid and finally alcohol, the precipitate formed being removed between each addition. The activities of the various fractions were measured for two days, and then the quantity of lead sulphate in each fraction was weighed. By dividing the β-activity at any time, after the maximum is reached, measured by the ordinate at that time, by the weight of lead sulphate, the concentration of thorium-*B* in lead sulphate at that time is obtained.

| No. of precipitate. | Weight of lead sulphate. Gram. | Activity at 5 p.m. | Activity per gram of lead sulphate at 5 p.m. | Activity at 11 a.m. next day. | Activity per gram at 11 a.m. next day. |
|---|---|---|---|---|---|
| 1 | 0·1161 | 0·90 | 7·25 | 0·29 | 2·496 |
| 2 | 0·2879 | 2·086 | 7·26 | 0·68 | 2·360 |
| 3 | 0·1810 | 1·28 | 7·09 | 0·374 | 2·064 |
| 4 | 0·0894 | 0·65 | 7·29 | 0·225 | 2·51 |
| 5 | 0·0501 | 0·456 | 9·1 | 0·15 | 2·99 |

The last two columns are merely confirmatory evidence of the constant distribution of thorium-*B* throughout the lead. Lead was fractionally crystallised as chloride, and also fractionally volatilised as chloride, and in each case similar series to the one shown above were obtained, showing that it was not possible to alter the concentration of thorium-*B* in lead.

Thorium-*C* was fractionally precipitated with bismuth in two ways. The bismuth was dissolved in concentrated ammonium carbonate, and then reprecipitated by boiling. In every experiment that was made a very small concentration from the bismuth was observed in the opposite sense to that which would have occurred with polonium. The second method was by fractional precipitation of the oxychloride, and again a very small concentration was observed, thorium-*C* being more soluble than bismuth. The concentration of the first portion was 1·735 units of activity per gram of bismuth oxide, whilst that of the second portion was 1·88. The difference in concentration is very small, and is probably capable of the simple explanation that there is present a small quantity of thorium-*B* which produces thorium-*C* in the interval between the precipitations.

### *Radium*-B *and Radium*-C.

In the same way as has been shown with thorium-*B* and -*C*, radium-*B* and -*C* were found to be similar to lead and bismuth respectively, to the exclusion of all other elements. A solution of the active deposit of rapid change, containing in addition lead and bismuth, was treated in the following ways so that these two metals were separated:

(1) Lead precipitated as lead sulphate, bismuth precipitated as bismuth sulphide.

(2) Lead precipitated as chloride.

(3) Bismuth precipitated as bismuth oxychloride, lead as lead hydroxide.

(4) Bismuth precipitated with *m*-nitrobenzoic acid.

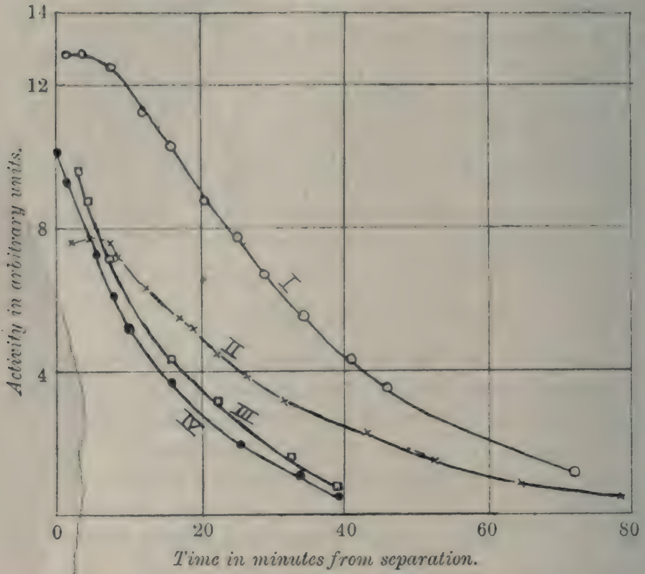
(5) Bismuth precipitated as metal on the cathode, lead precipitated as lead peroxide on the anode.

The curves obtained (see Fig. 2) show that the activity of the lead precipitates decay to half value in thirty-six minutes, whilst the bismuth precipitates decay to half value in from twenty to twenty-two minutes, showing that the activities, in the first case, were due to radium-*B*, and in the second case, to radium-*C*. If the preparation of radium-*B* is pure initially, the activity ought to rise to a maximum in 32·87 minutes after separation. The form of the curves showed that the activities of the substances contained in the lead was falling from a maximum value, but even by precipitating lead sulphate, collecting it, and drying it within ten minutes it was not possible to get a very definite rise to a maximum.

Owing to the shortness of the periods of both substances it was found impossible to make determinations of their behaviour on fractional treatment.

The results of these experiments are therefore that in all the reactions which it was possible to try it was observed that radium-*B* behaves as lead, and that radium-*C* behaves as bismuth. Considering the known similarity between the corresponding members of the active deposit groups, it is most probable that radium-*B* and radium-*C* are chemically non-separable from lead and bismuth in the same way as thorium-*B* and thorium-*C* have been shown to be.

FIG. 2



Curve I: *Activity obtained in lead sulphate—Radium*-B.
,, II: *Activity of lead peroxide on anode—Radium*-B.
,, III: *Activity of bismuth on cathode—Radium*-C.
,, IV: *Activity of ppt. with* m-*nitrobenzoic acid—Radium*-C.

### *Actinium*-B *and Actinium*-C.

In the case of these two substances the same experiments were made as with radium-*B* and radium-*C*, and it was observed that similarly they were like lead and bismuth respectively.

The activity of the lead precipitated from a solution of actinium active deposit either as lead sulphate, lead chloride, lead sulphide, or lead peroxide on the anode decayed to half value in thirty-eight minutes. In this case the activity of a lead precipitate, if it, initially, contains pure actinium-*B*, should reach a maximum value in 9·29 minutes. It was not possible to observe this maximum, and all the precipitates obtained were, by the time they could be dried and measured, decaying exponentially.

The decay of actinium-*C* could be measured in bismuth obtained as a precipitate with *m*-nitrobenzoic acid or by deposition of metallic bismuth on the cathode. Bismuth which was obtained in this way had an activity which decayed to half value in something less than three minutes. These measurements were made with α-rays. Enough actinium was not available to obtain a sufficient quantity of the products for β-ray measurements, so that it is, at the moment, not possible to say anything about the chemical behaviour of actinium-*D*.

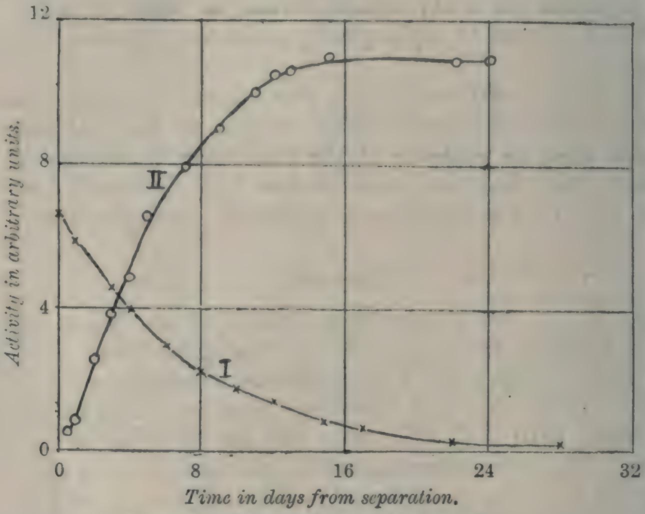
The conclusions that were drawn with respect to radium-*B* and -*C* are equally applicable here, namely, that in all the reactions that have been tried no evidence of the separation of actinium-*B* and actinium-*C* from lead and bismuth has been obtained, and it is probable that they are chemically similar to these elements.

### *Radium*-E.

Radium-*E* was for a long time considered to be a complex substance owing to the work of Rutherford (*Phil. Mag.*, 1904, [vi], **8**, 636) and of Meyer and von Schweidler (*Sitzungsber. K. Akad. Wiss. Wien*, 1906, ii*a*, **115**, 697), but later work due to Antonoff (*Phil. Mag.*, 1910, [vi], **19**, 825) has shown it to be a single substance. This work shows that a substance with a period of average life of 7·25 days followed radio-lead, but no evidence has yet been given to show whether polonium is the direct product of radium-*E*.

A sample of radio-lead containing large quantities of lead was precipitated with sulphuric acid. By one precipitation radio-lead is freed from about 80 per cent. of its β-ray activity. By dissolving this sulphate in ammonium acetate, reprecipitating with hydrogen sulphide, redissolving in acid, and finally reprecipitating with sulphuric acid, radio-lead is obtained practically free from β- or α-ray activity. Measurements were then made with the apparatus used by Soddy (*Phil. Mag.*, 1909, [vi], **18**, 858) to attempt to detect a growth of α-radiation from uranium-*X*, in which the powerful β-radiation was suppressed by placing the preparation between the poles of a magnet. The electroscope was of brass, and had in its base an opening 9 cm. long by 1·75 cm. broad, which was covered with aluminium foil 0·0031 mm. thick. Across this opening, arrangements were made for pushing over or withdrawing a piece of mica 0·05 mm. thick. The preparations were on a thin layer of filter paper, contained in a tray 8 × 1·5 cm., which was placed between the poles of the electromagnet, and was 0·5 cm. below the aluminium foil. If the magnet was off and the mica foil across the opening, all the $\alpha$-rays would be absorbed, and only $\beta$-rays and a small quantity of $\gamma$-rays would reach the ionising chamber. If the magnet was on and the mica away from the opening, most of the ionising effect would be due to $\alpha$-rays, but there would be a small effect due to undeviated $\beta$-rays and the small quantity of $\gamma$-rays. The growth of $\alpha$- and $\beta$-rays from two preparations of radio-lead was measured with (1) radio-lead precipitated twice as lead sulphate, and (2) radio-lead crystallised twice as lead chloride. The curves agree with those calculated from the view that the only intermediate member between radium-*D* and radium-*F* is radium-*E* with a period of 7·25 days.

FIG. 3.



Curve I: *Decay of $\beta$-rays of radium*-E.
,, II: *Growth of $\alpha$-rays of radium*-F.
(Note.—Curve II is on a larger scale than Curve I.)

The simultaneous decay of radium-*E* and growth of polonium was also observed. The purest radium-*E* was obtained by separating by two crystallisations of lead chloride both radium-*E* and polonium from a relatively large quantity of radio-lead. The separation was then repeated after two days had elapsed, and the last fractions of lead were removed as sulphate. A rod of bismuth was then immersed in the filtrate for three or four hours. In this way a strong $\beta$-ray preparation with an $\alpha$-activity less than one-tenth of the $\beta$-ray activity was obtained. The $\beta$-ray activity decayed to half value in five days, whilst the $\alpha$-ray activity increased according to the $I_t/I_\infty = 1 - e^{-\lambda t}$ law, showing that the $\alpha$-ray substance was produced directly from radium-*E*. There is thus no evidence of any intermediate substances except radium-*E* between radio-lead and polonium (see Fig. 3).

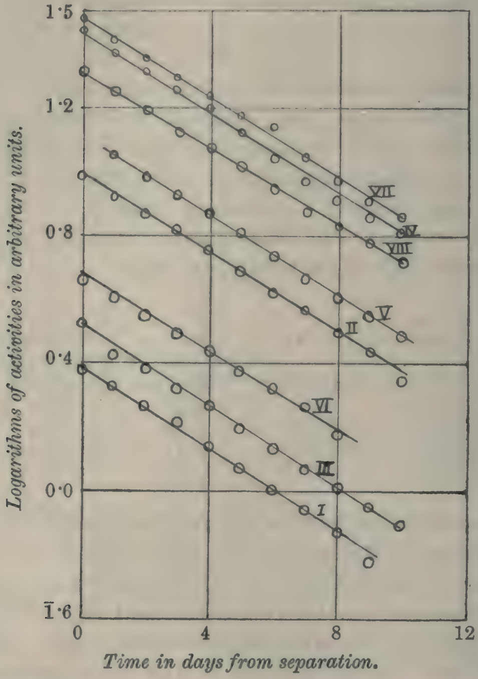
The chemical nature of radium-*E* was then studied, and it was found to be in all respects similar to bismuth. It was found to remain with the bismuth when that substance was precipitated, after the removal of the lead from a radio-lead solution, by hydrogen sulphide, ammonia, or dilute ammonium carbonate, and with the bismuth when that element was precipitated from a radio-lead solution by *m*-nitrobenzoic acid or as bismuth oxychloride. Fractional precipitation experiments were also made by precipitating, by boiling, bismuth carbonate dissolved in concentrated ammonium carbonate. The decay curves were taken, and then the bismuth estimated gravimetrically as oxide.

| No. of precipitate. | Weight of bismuth oxide. Gram. | Activity of precipitate on October 23rd. | Activity per gram on that date. | Activity of precipitate on October 29th. | Activity per gram on that date. |
|---|---|---|---|---|---|
| 1 | 0·1399 | 3·732 | 2·67 | 1·536 | 1·099 |
| 2 | 0·0920 | 2·377 | 2·58 | 1·033 | 1·120 |
| 3 | 0·0496 | 1·323 | 2·72 | 0·6054 | 1·215 |
| 4 | 0·0125 | 0·3356 | 2·68 | 0·1356 | 1·084 |

The last two columns confirm the regular decay of radium-*E*.

The conclusions of Rutherford already referred to concerning the complex nature of radium-*E* were arrived at by a consideration of the activities shown by the volatilised and unvolatilised parts of radium-*E* collected from radium emanation on a platinum wire. Experiments were therefore made in the volatilisation of bismuth compounds, for example, bismuth sulphide, bismuth chloride, and bismuth iodide. A strong preparation of radium-*E* had a little bismuth added to it, the whole being dissolved, precipitated as carbonate, and ignited in the filter paper, so that the oxide was reduced to metal. This was thoroughly ground with a quantity of iodine, placed at the bottom of a long, hard glass test-tube, and heated. Bismuth iodide was formed, which volatilised and condensed over a considerable length of tube. The tube was then divided into a number of sections. One section had a particularly strong activity, and the volatilisation process was repeated for it alone. In this way eight fractions were obtained, the radiation of which without exception decayed to half value in from 5·0 to 5·2 days. The logarithmic curves are given in Fig. 4. As the total quantity of bismuth was equivalent to only about 0·05 gram of bismuth oxide, the amount of bismuth in each fraction was very small, and thus it was not possible to get an exact determination of the concentration of radium-*E*, but there was no distinct alteration in the proportion of radium-*E* to bismuth in any of the fractions. Had there been any other substance present, such as a second intermediate substance between radio-lead and polonium, it would have shown itself in a difference between the decay curves of the first and last fractions. No such difference was observed.

FIG. 4.



*Lines are logarithmic decay curves of radium-*E*, and are numbered in the order of the volatilities.*

## *Summary.*

It has been shown that uranium-*X* and radio-actinium are chemically similar to, and non-separable from, thorium; mesothorium-2 is non-separable from actinium; thorium-*B* is non-separable from lead; radium-*B* and actinium-*B* are extremely similar to lead, and most probably non-separable from it; thorium-*C*, radium-*C*, and actinium-*C* are very closely allied to bismuth, and probably chemically similar to it. The present view that there is only one product, namely, radium-*E*, between radio-lead and polonium, has been confirmed by the direct measurement of the growth of radium-*F* from radium-*E*; finally, radium-*E* has been shown to possess chemical properties identical with those of bismuth in all respects.

I desire to thank Mr. F. Soddy, F.R.S., for suggesting this research, for his interest in it throughout its entire course, and for the use of materials employed in carrying it out.

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# XLVII.—*The Identification of Ipuranol and Some Allied Compounds as Phytosterol Glucosides.*

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

THE compound designated as ipuranol was first isolated in these laboratories in 1908 from the stems of *Ipomoea purpurea*, Roth (Nat. Ord. *Convolvulaceae*), received from South Africa (*Amer. J. Pharm.*, 1908, **80**, 264). The amount of substance obtained from this source was so small as to permit only of determining its empirical composition, melting point (285—290°), and the melting point of its acetyl derivative (160°). At about the same time, however, an evidently identical substance was isolated from olive bark (T., 1908, **93**, 907), and as in this instance both the substance (m. p. 285—290°) and its well-crystallised acetyl derivative (m. p. 160°) were analysed, it was concluded that ipuranol is a dihydric alcohol, possessing the formula $C_{23}H_{38}O_2(OH)_2$. The analytical figures obtained for both these compounds were, in fact, in excellent agreement with this assumption. In the same year a very small amount of a similar substance was obtained from nutmeg (*Amer. J. Pharm.*, 1908, **80**, 575), which, however, could only be obtained sufficiently pure for analysis in the form of its acetyl derivative (m. p. 163—164°). It was first in this connexion that the substance was observed to yield a colour reaction similar to that given by the phytosterols.

In the intervening years a considerable further number of substances have been isolated from widely different sources, which either agreed in composition with the formula assigned to ipuranol, or which differed from the latter in their characters and composition only to such an extent as to cause them to be regarded as homologous compounds. To these apparently related substances the following distinctive names and formulæ were assigned: citrullol, $C_{22}H_{36}O_2(OH)_2$, melting at 285—290° (T., 1910, **97**, 102), and trifolianol, $C_{21}H_{34}O_2(OH)_2$, melting at 295° (T., 1910, **97**, 249). These two substances, together with ipuranol, were thus considered to be members of a series of dihydric alcohols, represented by the general formula $C_nH_{2n-6}O_4$.

Another group of substances had meanwhile been obtained, which were likewise regarded as dihydric alcohols, and yielded colour reactions similar to those given by the phytosterols. These compounds, however, differed appreciably from the members of the ipuranol series by their greater facility of crystallisation and a generally lower melting point, as also to some extent in their percentage composition. The first member of this class of compounds was isolated from jalap tubers (*Ipomoea purga*, Hayne), and to it the name ipurganol (m. p. 222—225°) and the formula $C_{21}H_{32}O_2(OH)_2$ were respectively assigned (*J. Amer. Chem. Soc.*, 1910, **32**, 89). Various closely related substances which, together with ipurganol, appeared to constitute a series of dihydric alcohols represented by the general formula $C_nH_{2n-8}O_4$, were given the following distinctive names and formulæ: bryonol, $C_{22}H_{34}O_2(OH)_2$, melting at 210—212° (T., 1911, **99**, 943); grindelol and anonol, $C_{23}H_{36}O_2(OH)_2$, melting at 256—257° and 294—298° respectively (*Proc. Amer. Pharm. Assoc.*, 1907, **55**, 342, and *Pharm. J.*, 1911, **87**, 744); and cucurbitol, $C_{24}H_{38}O_2(OH)_2$, melting at 260° (*J. Amer. Chem. Soc.*, 1910, **32**, 36). A substance, melting at 245°, to which the name of calabarol has been given (T., 1911, **99**, 2155), was considered to possess the formula $C_{23}H_{34}O_2(OH)_2$, and therefore to be the first representative of dihydric alcohols having the general formula $C_nH_{2n-10}O_4$.

Quite recently Tutin and Clewer (T., 1912, **101**, 2230) isolated from *Cluytia similis*, Muell. Arg. (Nat. Ord. *Euphorbiaceae*), a substance which was observed to resemble ipuranol and other related compounds in its general characters, and was designated cluytianol. It was subsequently obtained in larger amount from taraxacum root (T., 1912, **101**, 2426). This substance (m. p. 300—305°) was first regarded as a trihydric alcohol, $C_{23}H_{37}O(OH)_3$ (P., 1912, **28**, 265), but a comparison of the figures obtained by its analysis and the analysis of its acetyl and benzoyl derivatives, together with a molecular-weight determination of the acetyl derivative, subsequently led the above-mentioned authors to regard cluytianol as a tetrahydric alcohol, having the formula $C_{29}H_{46}O(OH)_4$ (P., 1912,

**23**, 317). At the same time, and with similar considerations, ipuranol was thought to be more correctly represented as a trihydric alcohol, having the formula $C_{29}H_{47}O_2(OH)_3$, instead of $C_{23}H_{38}O_2(OH)_2$, as originally adopted.

The amounts of the various above-mentioned compounds which have hitherto been isolated were in most cases comparatively small, and, with a few exceptions, did not permit of the analysis of their derivatives. The characters of the substances nevertheless rendered it evident that they represented a new class of compounds, and as they gave well-crystallised acetyl and benzoyl derivatives, having definite melting points, it was apparent that they were of alcoholic nature. It may also be noted that, although ipuranol was first obtained from an ethyl acetate extract of the resinous constituents of the respective plant, it has subsequently, as well as the related compounds, been isolated either from the petroleum or the ether extract of the resin. In one instance (citrullol, *loc. cit.*), the substance was separated from an aqueous liquid, in which it appeared to be contained in a colloidal state. Furthermore, in a considerable number of cases the various compounds were isolated from a petroleum extract of the resinous constituents after the extract had been heated for some time with an alcoholic solution of potassium hydroxide, and this fact seemed especially to confirm the view respecting the alcoholic nature of the compounds.

It has naturally been deemed desirable to obtain, if possible, some further information regarding the character of the numerous compounds here considered, but the small amounts of material hitherto available had precluded any extended experiments in this direction. Some recent observations, however, have served to reveal the nature of the compounds in question, inasmuch as it has been found that several of them, when heated in amyl-alcoholic solution with aqueous hydrogen chloride, become hydrolysed with the formation of a phytosterol and dextrose. It is thus evident that the substances are phytosterol glucosides, and their percentage composition is also in harmony with this view.

In order that the results obtained by the analysis of these various compounds and some of their derivatives, as previously recorded, may be compared with the calculated percentage figures for phytosterol glucosides and the respective acetyl and benzoyl derivatives of the latter, they have been arranged in a tabular form, and at the same time the source of the compounds has been indicated, together with the names and formulæ hitherto assigned to them.

In addition to the list on p. 402, substances resembling ipuranol have also been obtained from the fruit of *Ecballium Elaterium*

(T., 1909, **95**, 1988) and from the bark of *Erythrophloeum Guineense* (*Amer. J. Pharm.*, 1912, **84**, 348), but not in amounts sufficient for analysis.

| Name and formula. | | Source. | M.p. and analysis. | | M. p. and analysis of acetyl derivative. | |
|---|---|---|---|---|---|---|
| | | | | C. H. | | C. H. |
| Ipuranol, | $C_{23}H_{40}O_4$ | *Ipomoea purpurea* .......... | 285—290°. | 72·6 ; 10·6 | 160°. | — |
| ,, | ,, | Olive bark.................. | 285—290°. | 72·6 ; 10·6 | 160°. | 69·8 ; 9·4 |
| ,, | ,, | Nutmeg .................... | — | — | 163—164°. | 69·5 ; 9·4 |
| ,, | ,, | *Prunus serotina*, bark ...... | 285—290°. | 72·3 ; 10·7 | 160°. | — |
| ,, | ,, | ,, ,, leaves .... | 295°. | — | 163°. | — |
| ,, | ,, | *Apocynum androsaemifolium* | 285—290°. | 72·4 ; 10·5 | 162°. | — |
| ,, | ,, | *Rumex Ecklonianus* ........ | 285—290°. | — | 162°. | — |
| ,, | ,, | *Ornithogalum thyrsoides* .... | 285—290°. | 72·3 ; 10·5 | 162°. | — |
| ,, | ,, | *Gelsemium sempervirens* .... | 290°. | 72·3 ; 10·5 | 162°. | — |
| ,, | ,, | *Iris versicolor* .............. | 285—290°. | 72·3 ; 10·3 | 162—163°. | — |
| ,, | ,, | *Withania somnifera* ........ | 285—290°. | 72·4 ; 10·3 | 164—165°. | — |
| ,, | ,, | *Buphane disticha* .......... | 286°. | — | — | — |
| ,, | ,, | *Oenanthe crocata* .......... | 285—290°. | — | 161°. | — |
| ,, | ,, | *Casimiroa edulis* ............ | 280—285°. | 72·6 ; 10·4 | 166°. | 69·7 ; 9·5 |
| ,, | ,, | *Ipomoea orizabensis* ......... | 285—290°. | 72·4 ; 10·6 | 162°. | — |
| ,, | ,, | Scammony root............. | 285—290°. | 72·2 ; 10·6 | 162°. | — |
| Citrullol, | $C_{22}H_{38}O_4$ | Colocynth ................. | 285—290°. | 72·0 ; 10·6 | 167°. | 69·3 ; 9·2 |
| ,, | ,, | *Euonymus atropurpureus*.... | 285—290°. | 71·9 ; 10·7 | 164—165°. | 69·0 ; 9·3 |
| ,, | ,, | *Caulophyllum thalictroides*.. | 275—280°. | 71·9 ; 10·4 | 169—170°. | — |
| Trifolianol, | $C_{21}H_{36}O_4$ | *Trifolium pratense*.......... | 295°. | 71·4 ; 10·4 | 165—166°. | 68·8 ; 9·2 |
| ,, | ,, | ,, *incarnatum* ...... | 295—300°. | 71·6 ; 10·4 | 165—166°. | 68·6 ; 9·2 |
| Calabarol, | $C_{23}H_{36}O_4$ | Calabar bean ............... | 245°. | 73·1 ; 10·1 | — | — |
| Ipurganol, | $C_{21}H_{34}O_4$ | *Ipomoea purga*.............. | 222—225°. | 71·7 ; 10·0 | 166—167°. | 68·9 ; 8·8 |
| Bryonol, | $C_{22}H_{36}O_4$ | Bryony root ................ | 210—212°. | 72·3 ; 10·1 | 152°. | 69·1 ; 9·0 |
| Grindelol, | $C_{23}H_{38}O_4$ | *Grindelia camporum* ........ | 257°. | 72·7 ; 10·2 | 161°. | — |
| Anonol, | $C_{23}H_{38}O_4$ | *Anona muricata* ............ | 294—298°. | 72·9 ; 10·3 | 166°. | — |
| Cucurbitol, | $C_{24}H_{40}O_4$ | Watermelon seed ........... | 260°. | 73·2 ; 10·4 | 150°. | — |
| Cluytianol, | $C_{29}H_{50}O_5$ | *Cluytia similis* ............ | 300—305°. | 72·8 ; 10·5 | 160°. | 68·7 ; 9·1 |
| ,, | ,, | Taraxacum root ............ | 297°. | 72·5 ; 10·6 | 161°. | 68·6 ; 9·1 |

In a few instances benzoyl derivatives of the above-mentioned compounds were prepared, which had the following characters: Benzoylipuranol, from *Oenanthe crocata* and *Casimiroa edulis*, melting at 196° and 197° respectively; benzoylanonol, m. p. 197—198°. C=75·9; H=7·8; benzoylcalabarol, m. p. 195—196°. C=76·1; H=7·8; benzoylcluytianol (from *Cluytia similis*), m. p. 192°. C=76·3; H=7·7; (from taraxacum root), m. p. 196°. C=76·2; H=7·9 per cent.

It is well known that a considerable number of isomeric phytosterols occur in nature which possess the formula $C_{27}H_{46}O$, whilst other compounds of this type are represented by the formula $C_{30}H_{50}O$ (or $C_{30}H_{48}O$) and $C_{20}H_{34}O$. As examples of these different classes there may be noted: sitosterol, $C_{27}H_{46}O$ (*Monatsh.*, 1897, **18**, 551), stigmasterol, $C_{30}H_{50}O$ or $C_{30}H_{48}O$ (*Ber.*, 1906, **39**, 4378), and rhamnol, $C_{20}H_{34}O$ (*Proc. Amer. Pharm. Assoc.*, 1904, **52**, 299). The glucosides and their acetyl and benzoyl derivatives of the first two types of phytosterols mentioned would have the following composition respectively:

### *Sitosterol Glucoside and Derivatives.*

$C_{33}H_{56}O_6$ requires C=72·3; H=10·2 per cent.
$C_{33}H_{52}O_6(CO{\cdot}CH_3)_4$ requires C=68·7; H=8·9 per cent.
$C_{33}H_{52}O_6(CO{\cdot}C_6H_5)_4$ ,, C=75·9; H=7·5 ,, ,,

### *Stigmasterol Glucoside and Derivatives.*

$C_{36}H_{60}O_6$ requires C=73·5; H=10·2 per cent.
$C_{36}H_{56}O_6(CO{\cdot}CH_3)_4$ requires C=69·8; H=9·0 per cent.
$C_{36}H_{56}O_6(CO{\cdot}C_6H_5)_4$ „ C=76·5; H=7·6 „ „

A comparison of these figures with those afforded by the analysis of the above-mentioned, naturally occurring compounds renders it probable that a considerable proportion of the latter are glucosides of sitosterol or one of its isomerides, whilst in some cases their composition would appear to approximate more closely to that of a stigmasterol glucoside. Inasmuch as different phytosterols are frequently found in the same plant, it is to be expected that their respective glucosides may also occur in the form of mixtures, and these would be exceedingly difficult to separate. The possibility of different sugars being united with the phytosterol complex is also not excluded.

In this connexion it may incidentally be noted that H. and A. Euler (*Ber.*, 1907, **40**, 4762) obtained from the varnish-like coating of the leaves of the common alder (*Alnus glutinosa*, Gaertn.) a substance which they designated glutinolic acid, and which was stated to give an intense cholesterol (phytosterol) reaction. To this substance, which was obtained only in an amorphous state, they assigned the formula $(C_{28}H_{48}O_5)_x$, which requires C=72·4; H=10·3 per cent. These figures are in such close agreement with those required for a sitosterol glucoside that, together with the colour reaction noted, it appears probable that the so-called "glutinolic acid" consisted essentially of a compound of the above-described type. The method by which the substance was obtained, together with its low melting point, likewise suggests that the observed acidic properties may have been due to its contamination with a small amount of a fatty acid.

## EXPERIMENTAL.

It had previously been observed that some of the compounds under consideration were not altered by heating with aqueous hydrogen chloride in the presence of a little alcohol, but this result was evidently due to their sparing solubility, and did not preclude the possibility of their being glucosidic. As the compounds, however, were soluble in warm amyl alcohol, it was found that their hydrolysis could be effected by the use of this solvent. Such of them as were at present available in sufficient amounts have therefore now been examined in the direction indicated, and with the following results:

I. *Ipuranol* (m. p. 290—295°). A typical specimen of this substance had the following composition:

0·1147 gave 0·3039 $CO_2$ and 0·1084 $H_2O$. C = 72·3; H = 10·5.

The formula originally assigned to ipuranol, namely, $C_{23}H_{40}O_4$, requires C = 72·6; H = 10·5 per cent.

Sitosterol glucoside, $C_{33}H_{56}O_6$, requires C = 72·3; H = 10·2 per cent.

Half a gram of the substance was dissolved in 30 c.c. of hot amyl alcohol, and 10 c.c. of an aqueous 15 per cent. solution of hydrogen chloride added, together with sufficient ethyl alcohol to form a homogeneous liquid. After heating for two hours in a reflux apparatus, steam was passed through the mixture to remove the amyl alcohol, and the contents of the flask then filtered. A solid substance was thus collected, which, when crystallised from a mixture of alcohol and ethyl acetate, separated in glistening leaflets melting at 136°. This substance gave the phytosterol colour reaction, and it evidently belonged to that class of compounds:

0·1041 gave 0·3204 $CO_2$ and 0·1127 $H_2O$. C = 83·9; H = 12·0.
$C_{27}H_{46}O$ requires C = 83·9; H = 11·9 per cent.

The aqueous acid liquid, from which the phytosterol had been separated by filtration, was exactly neutralised with sodium carbonate, evaporated to dryness, the residue digested with absolute alcohol, and the mixture filtered. On evaporating the alcoholic filtrate a small amount of a syrupy residue was obtained, which reduced Fehling's solution, and yielded an osazone melting and decomposing at 212°. It was thus evident that the sugar consisted of dextrose.

The original compound had thus become resolved by hydrolysis into a phytosterol and dextrose, according to the equation:

$$C_{33}H_{56}O_6 + H_2O = C_{27}H_{46}O + C_6H_{12}O_6.$$

II. *Ipuranol* (m. p. 280—285°). This specimen of the substance was obtained from a different source from the preceding one, and it gave on analysis the following result:

0·0973 gave 0·2573 $CO_2$ and 0·0918 $H_2O$. C = 72·1; H = 10·5.
$C_{33}H_{56}O_6$ requires C = 72·3; H = 10·2 per cent.

Half a gram of this substance was hydrolysed in the manner above described, when it yielded a phytosterol, which separated in glistening leaflets, melting at 136°. This was analysed, and its specific rotatory power determined:

0·0911 gave 0·2800 $CO_2$ and 0·1002 $H_2O$. C = 83·8; H = 12·2.
$C_{27}H_{46}O$ requires C = 83·9; H = 11·9 per cent.

0·2649 of anhydrous substance, made up to 20 c.c. with chloroform, gave $\alpha_D$ $-0°56'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-35·2°$.

The aqueous acid liquid obtained by the hydrolysis was found to contain a sugar, from which *d*-phenylglucosazone (m. p. 212°) was prepared.

III. *Citrullol* (m. p. 285—290°). This represented the compound which had previously been isolated from colocynth (T., 1910, **97**, 102). A small amount (0·15 gram) of its acetyl derivative was hydrolysed in the above-described manner, when it yielded a phytosterol which separated from a mixture of alcohol and ethyl acetate in small needles, melting at 145—149°. The sugar produced by the hydrolysis gave an osazone which, in the crude state, melted at 190—192°, but the amount was too small to permit of its purification.

IV. *Bryonol* (m. p. 210—212°). The compound to which this name had been assigned was obtained from bryony root (T., 1911, **99**, 943). A small amount (0·15 gram) of the substance, when hydrolysed in the manner above described, yielded a phytosterol which separated from a mixture of alcohol and ethyl acetate in leaflets, melting at about 90—100°. When recrystallised from alcohol it was obtained in small tufts of needles, which sintered at 90° and melted completely at 105°. The same melting point was observed after it had been kept in a vacuum desiccator for forty-eight hours. The phytosterol dissolved completely in concentrated sulphuric acid with a yellow colour and green fluorescence, and evidently differed from sitosterol. A small amount of sugar was likewise produced by the hydrolysis, and this was found to reduce Fehling's solution, but it was not sufficient for the preparation of an osazone.

V. *Cluytianol* (m. p. 297°). The specimen of this compound which served for its present examination was obtained from taraxacum root (T., 1912, **101**, 2426). A small amount (0·2 gram) of the substance was hydrolysed as above described, when it yielded a phytosterol which crystallised in glistening leaflets, melting at 136°. The sugar produced by the hydrolysis was found to reduce Fehling's solution, but was not sufficient in amount for the preparation of an osazone.

Although it has not been possible to subject all the compounds enumerated in the preceding list to the above-described treatment, the results which are now recorded are deemed quite sufficient to lead to the conclusion that they are all phytosterol glucosides. Such compounds had not previously been known to occur in nature, and it may be regarded as of some significance that in practically all instances where their isolation had been effected phytosterols of varying character had also been found. With consideration of the facts which have thus been elicited respecting the nature of the compounds in question, it is not deemed desirable that distinctive names should be perpetuated for them, but that they should receive some collective designation, and it is therefore proposed that they be termed *phytosterolins.* The future examination of compounds of this type, when available in sufficient amounts, would appear to be most suitably directed to the characterisation of the phytosterols which they yield on hydrolysis, and also, when possible, to that of the sugar produced.

It may finally be noted that some recent experiments, conducted by one of us, have led to the synthesis of sitosterol-*d*-glucoside, which has been found to possess properties agreeing with those of the substance designated as ipuranol. The details of these experiments will form the subject of a further communication.

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## XLVIII.—*The Absorption Spectra of Substances Containing Labile Hydrogen Atoms.*

By PETER JOSEPH BRANNIGAN, ALEXANDER KILLEN MACBETH, and ALFRED WALTER STEWART.

THE absorption spectra of ethyl acetoacetate and some of its derivatives were examined by Magini (*Atti R. Accad. Lincei*, 1904, [v], **13**, i, 104), and by Baly and Desch (T., 1904, **85**, 1029; compare T., 1905, **87**, 766). The last-named authors put forward certain views to account for their results. This work has been repeated and much extended by Hantzsch (*Ber.*, 1910, **43**, 3049), who has thrown very grave doubt on the assumptions made by Baly and Desch. In the present paper the spectra of various compounds which contain hydrogen atoms replaceable by sodium have been examined with the view of increasing our knowledge of simple substances containing such groupings. The results obtained tend to confirm the correctness of Hantzsch's views.

Baly and Desch observed that in alcoholic solution ethyl acetoacetate shows only general absorption; the enolic derivative, ethyl ethoxycrotonate, $CH_3\cdot C(OEt)\!:\!CH\cdot CO_2Et$, shows no selective absorption; nor does what they call "the keto-substance ethyl ethylacetoacetate," $CH_3\cdot CO\cdot CHEt\cdot CO_2Et$. When, however, alkali is added to an alcoholic solution of ethyl acetoacetate an absorption band appears in the spectrum, and attains greater and greater persistence as the relative amount of alkali present is increased, until at last a maximum persistence of band is obtained, beyond which no further change in the spectrum occurs, even when more alkali is added to the solution. Similar bands were found in the spectra of metallic derivatives of acetylacetone and the aluminium derivative of ethyl acetoacetate. From their results, Baly and Desch put forward the idea that the presence of the bands should be ascribed to an oscillation between the enolic and ketonic forms; and that the rôle of the alkali is to increase the rate of change, that is, to increase the number of molecules in the state of change. They had observed that hydrochloric acid has not the same effect as alkali; and this they accounted for by stating that "hydrochloric acid should have an exactly opposite effect, owing to the restraining influence it is known to exert on certain of these changes."

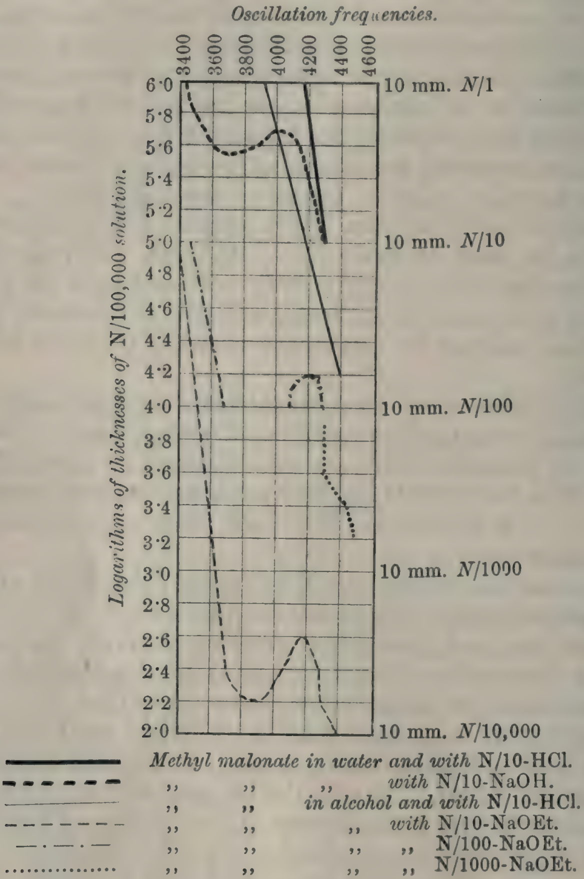
With regard to the latter part of the subject, it is sufficient to point out that the work of Knorr (*Ber.*, 1911, **44**, 1150) on ethyl acetoacetate conclusively proves that both acids and bases have the same influence in the case of the transformation of the enolic into the ketonic form; so that the assumption made by Baly and Desch is unfounded.

Further, K. H. Meyer (*Annalen*, 1911, **380**, 212) has shown by purely chemical means that both enolic and ketonic forms of ethyl acetoacetate are present in ethyl-alcoholic solution; so that if Baly and Desch's views were correct, an absorption band should make its appearance in such a solution. No band, however, is observed under these conditions.

The cases of the hydrochloric acid solution and the solution of the pure ethyl acetoacetate having thus been disposed of, we come to the question of the bands produced in presence of alkali. Hantzsch (*loc. cit.*) has shown that if two solutions of ethyl acetoacetate in alcohol are taken, one of which is much more dilute than the other, it is necessary to add very much more alkali to the weak solution than to the more concentrated one in order to produce the same persistence in the band. This observation appears to dispose of any idea that the sodium ethoxide acts as a catalyst, and seems to point rather to the view that a hydrolysable salt is formed by the action of the alkali on the ethyl acetoacetate, this salt being more strongly decomposed at high dilutions, and hence requiring the addition of more alkali under these conditions in order to form the same amount of salt which is produced by less alkali in more highly concentrated solutions of the ester. Hantzsch suggests that the band produced by the addition of alkali is simply the spectrum of the alkali salt of ethyl acetoacetate, and this view is strengthened by the fact that the spectrum of the aluminium derivative of ethyl acetoacetate closely resembles that produced by the addition of alkali to the ethyl acetoacetate solution.

Our results with methyl malonate agree completely with this view. In Fig. 1 are shown the curves of methyl malonate dissolved in alcohol in the presence of sodium ethoxide. The pure ester in

FIG. 1.



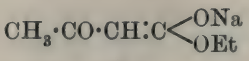
alcoholic solution shows no selective absorption, but a band is developed in presence of alkali, just as in the case of ethyl acetoacetate. It will be seen that if the sodium ethoxide is kept at a constant strength of $N/10$ all through the solutions whilst the ester is being more and more diluted, the complete broken-link curve is obtained. The dot-and-dash curve shows the result obtained when

*N*/100-methyl malonate is mixed with *N*/100-sodium ethoxide; and it will be seen that the beginning of the band (incomplete) occurs at a much higher concentration than is the case when more sodium ethoxide is present. Now suppose that the band is the absorption spectrum of the sodium derivative. It is clear that when there is a high concentration of sodium ethoxide there will be a considerable percentage of sodium derivative present per c.c.; and hence the solution must be greatly diluted before the band is produced. On the other hand, when less sodium ethoxide is present, owing to hydrolysis, there will be less of the sodium derivative present per c.c., and hence a thicker layer of solution must be employed in order to get the same absorption. This agrees entirely with our results, as can be seen from the curves. Again, the dotted line shows the result of further dilution. It represents the spectrum of *N*/1000-methyl malonate in the presence of *N*/1000-sodium ethoxide. In this case the hydrolysis of the sodium derivative will be greater still than before; and consequently a c.c. of the solution will contain very little of it, and will therefore be very diactinic, as is shown in the curve.

We have spoken of the "hydrolysis" of the salt, although our results might be just as easily explained by considering the chances of the formation of the sodium derivative under the mass-action law. Our results in aqueous solution, however, seem to justify our assumption. Under these conditions, as is well known, sodium derivatives such as these are much more readily decomposed than when dissolved in alcohol. We must therefore assume that in aqueous solution hydrolysis will be greater than in alcoholic solution; consequently, in order to have a given amount of sodium derivative present it will be necessary to employ much more concentrated solutions here than is necessary to do in alcoholic solutions. The curves in Fig. 1 show that this is actually the experimental result. In alcohol with *N*/10-sodium ethoxide present only a *N*/10,000-solution is required to show the band; whilst in water with *N*/10-sodium hydroxide present a *N*/10-solution of the malonate in approximately the same thicknesses is needed.

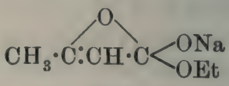
From these results, which agree with those obtained by Hantzsch in the case of ethyl acetoacetate, it seems evident that the band in these spectra has nothing whatever to do with the process suggested by Baly and Desch, but is merely due to the presence of the metallic derivative in solution.

We may now consider Hantzsch's views on this point. Since the enolic form of ethyl acetoacetate shows no band, whilst the sodium and aluminium derivatives manifest it, we are driven to conclude that there must be some constitutional difference between the enolic form and the sodium compound; for otherwise we should need to assume that two similarly constituted compounds have different spectra, which has not yet been found to be the case. Hantzsch examined two possible structures for the sodium derivative which are not derived from the true enolic form, and rejected the second



$CH_3\cdot CO\cdot CH\colon C\langle\begin{smallmatrix}ONa\\OEt\end{smallmatrix}$

(I.)

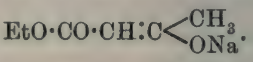


$CH_3\cdot \overset{O}{C\colon CH\cdot C}\langle\begin{smallmatrix}ONa\\OEt\end{smallmatrix}$

(II.)

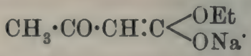
on the ground that it was too saturated a substance to show the great absorptive power exhibited by the sodium derivative of ethyl acetoacetate. The first formula he also rejected on the ground that it was almost identical (überaus ähnlich) with the normal enolic structure. A close examination will show that this is hardly justifiable without evidence. If we compare the two structures:

(I) **True enolic derivative,**



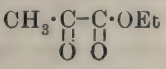
$EtO\cdot CO\cdot CH\colon C\langle\begin{smallmatrix}CH_3\\ONa\end{smallmatrix}.$

(II) **Hantzsch's formula,**

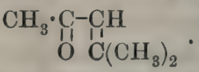


$CH_3\cdot CO\cdot CH\colon C\langle\begin{smallmatrix}OEt\\ONa\end{smallmatrix}.$

it will be seen that in the one case (II) there is a true carbonyl radicle, whilst in the other case (I) the carbonyl group of a carboxyl radicle is present, which shows no trace of carbonyl properties. It seemed quite possible that this difference might be sufficient to account for the difference in spectra; and we therefore endeavoured to find some compound containing the structure $\cdot CO\cdot CH\colon C\colon$, which occurs in (II). The simplest substance appeared to be mesityl oxide, $CH_3\cdot CO\cdot CH\colon C(CH_3)_2$, so we examined the spectrum of this substance, which is shown in Fig. 3. It will be seen that the structure $\cdot CO\cdot CH\colon C\colon$ does give rise to a band; but this band has its head at 3100, whereas the band in the spectrum of ethyl sodioacetoacetate occurs at 3700. On photographing mesityl oxide in the presence of alkali, we found that no change took place in its spectrum. This band in the mesityl oxide spectrum probably owes its appearance to a process similar to that which produces the band in the spectrum of ethyl pyruvate, as the two substances contain a similar system of double bonds:



$CH_3\cdot \underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}\cdot OEt$

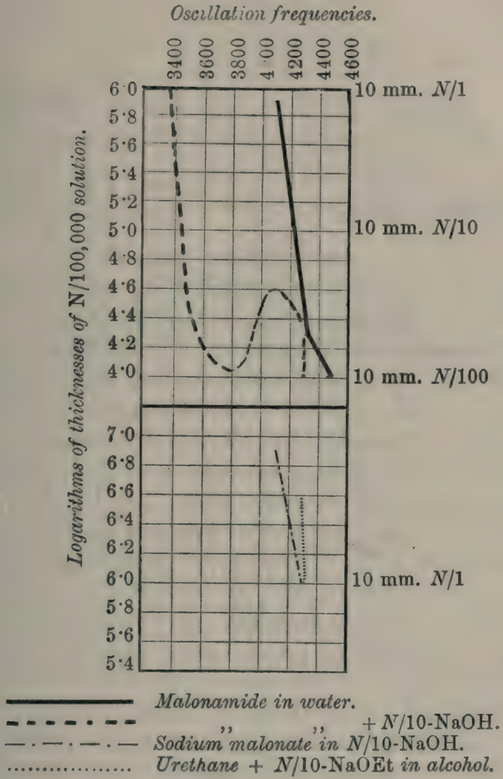


$CH_3\cdot \underset{O}{\underset{\|}{C}}-\underset{C(CH_3)_2}{\underset{\|}{CH}}.$

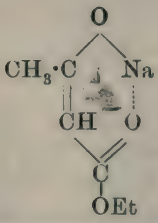
This is not an absolutely conclusive proof that the formula (II) above is not correct, but it seems sufficient.

We now come to Hantzsch's suggestion for a formula which differs sufficiently from the ordinary enolic form to account for the difference in spectra observed in practice. Hantzsch assumes that the metallic derivatives of ethyl acetoacetate are derived from the enolic form, but differ from it in that the metallic atom is played upon by the residual affinity of the carbonyl radicle in such a way

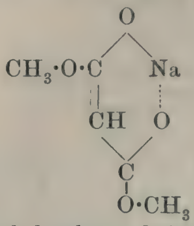
FIG. 2.



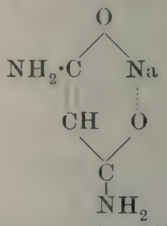
as to form an internal complex salt which may be represented thus:



the dotted line showing the residual affinity's attraction. This view necessitates the formation of a six-membered "ring" in the molecule, and we have endeavoured to see whether it stands the test in the malonic series as well as in the derivatives of ethyl acetoacetate. In the case of the sodium derivative of methyl malonate, the formation of the six-membered "ring" would be represented by the following formula:



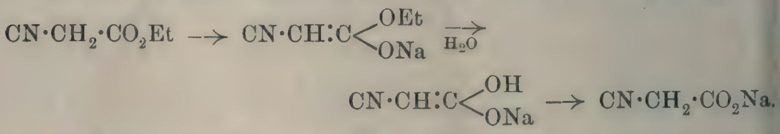
Methyl malonate derivative.



Sodium malonamide.

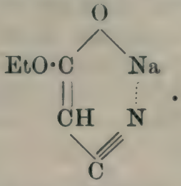
so that in this case the theory agrees with the facts. A similar "ring" might be produced in malonamide, which also shows an absorption band in the presence of alkali (see Fig. 2).

When ethyl cyanoacetate is considered, a reference to the curves in Fig. 3 will show that this substance behaves differently from those mentioned above. Instead of developing a band in the presence of sodium ethoxide, the compound shows only an increase in general absorptive power, although the rapid extension of its spectrum takes place in a region where the band occurs in the spectrum of methyl malonate in the presence of alkali. The curve of the absorption of ethyl cyanoacetate in aqueous solution shows but slight absorptive power, and no selective absorption is found when alkali is added to the solution. A consideration of the reactions of ethyl cyanoacetate throws some light on this abnormal behaviour. Although the substance is known to form a sodium derivative which can be obtained in alcoholic solution, this compound undergoes a peculiar decomposition in the presence of water, being converted into sodium cyanoacetate; and this change might best be accounted for by the following series of rearrangements:



$$CN\cdot CH_2\cdot CO_2Et \longrightarrow CN\cdot CH\colon C\!<\!\begin{smallmatrix}OEt\\ ONa\end{smallmatrix} \xrightarrow[H_2O]{} CN\cdot CH\colon C\!<\!\begin{smallmatrix}OH\\ ONa\end{smallmatrix} \longrightarrow CN\cdot CH_2\cdot CO_2Na.$$

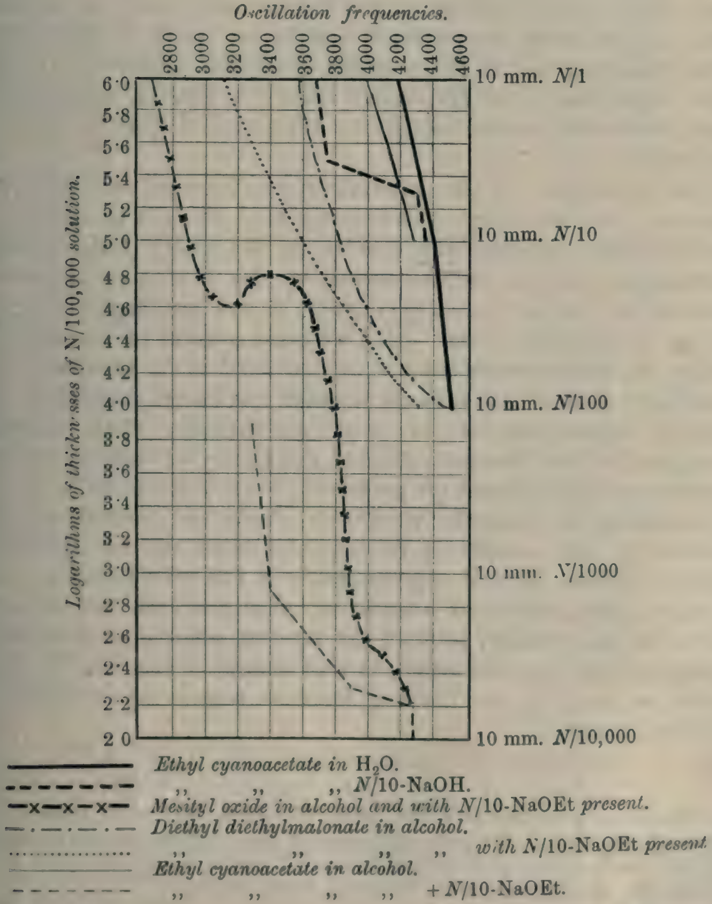
If we were to assume the structure of the sodium derivative to be $Na\cdot N\colon C\colon CH\cdot CO_2Et$, the change from ester to salt could not be accounted for so simply. We may reasonably make the assumption that the structure of the sodium derivative is that shown in the first set of formulæ, in which the sodium atom is attached to oxygen. If this be postulated, however, then the conditions necessary for Hantzsch's six-membered "ring" are not quite the same as in the previous cases, as there is no carbonyl radicle to attract the sodium atom, but instead of it we have the ·CN group:



This difference in the groups might very well be sufficient to produce an abnormality in the absorption spectrum; and thus the case rather strengthens Hantzsch's arguments.

We endeavoured to find another example of the same type, and

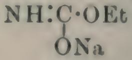
FIG. 3.



examined malonitrile. Unfortunately, this compound proved to be so readily oxidised, especially in the presence of alkali, that no trustworthy results could be obtained from it. We next photographed the spectrum of urethane, which yields a sodium derivative the structure of which might be either (I) or (II):

$Na{\cdot}NH{\cdot}CO_2Et$

(I.)



$NH{:}\underset{ONa}{\underset{|}{C}}{\cdot}OEt$

(II.)

In neither case is the formation of Hantzsch's six-membered "ring" possible, and as can be seen from the curve in Fig. 2 this body is very feebly absorbent, even in presence of sodium ethoxide.

The foregoing evidence appears to confirm the view that the bands in the spectra of substances capable of yielding a sodium derivative are due to the formation of an internal salt. The formation of the simple sodium salt alone is insufficient, as otherwise urethane and ethyl cyanoacetate would show bands in their spectra when photographed in the presence of sodium ethoxide. It therefore seems clear that Hantzsch's theory is correct, and that the previous attempt at the solution of the problem must be ruled out of account.

The assumption of the existence of the internal salt formation, however, does not carry us sufficiently far. It fails to account for the difference between the spectra of the enolic form of ethyl acetoacetate and the sodium derivative; for if it is to be assumed that sodium has an auxiliary valency, it will be illogical to refuse one to the hydrogen atom. Also, we must account for the fact that whilst ethyl β-chlorocrotonate shows no band in its spectrum, ethyl β-aminocrotonate * has a band in exactly the same position as that due to the sodium salt of ethyl acetoacetate. This difficulty disappears if we take into account the theory of valency recently put forward by Gebhard (*J. pr. Chem.*, 1911, [ii], **84**, 561).

According to Gebhard, when two atoms are united together directly by their maximum valency, the result can be represented as in (I) below. Now if any weakening in the bond between A and B takes place, the total amount of affinity of the two atoms is unaltered in quantity, so that the residual affinity must make its appearance on the two atoms as free affinity. This can be represented as in (II), and such a bond is termed by Gebhard an "ionised valency":

$$\underset{\text{(I.)}}{A\text{——}B} \qquad \underset{\text{(II.)}}{\cdots A\sim\sim\sim B\cdots} \qquad \underset{\text{(III.)}}{A^{+}\quad B^{-}}$$

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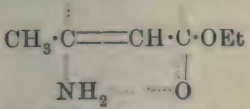
* The curves given by Baly and Desch (T., 1904, **85**, 1039) appear to be incorrectly numbered. We have photographed the spectrum of ethyl β-aminocrotonate and find that it is similar to curve 1 on the figure, not curve 3. It appears that the numbering of the curves has been inverted.

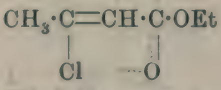
Case (III) represents the extreme state of dissociation, where the two atoms have separated from each other.

Now applying this idea to the case of ethyl β-aminocrotonate, the following result is obtained. It is well-established that the amino-group is very loosely held to the carbon, since it can be eliminated with great ease. This union should therefore be represented as being weaker than the full affinity of a single bond, and, consequently, we are led to postulate a superfluity of free affinity on the amino-group. This free affinity being in the 1:5-position with regard to the unsaturated carbonyl oxygen of the carboxyl group, will tend to interfere with the latter, and to this interaction of the two residual affinities we trace the origin of the band in the spectrum of the substance. In the case of ethyl β-chlorocrotonate the chlorine atom is by no means so labile as the amino-group in the amino-ester, so that we are justified in concluding that it is bound to the carbon by an ordinary unweakened bond. There will therefore be little free affinity on the chlorine, and hence there will be no play of unsaturations such as occurs in the other case. The same reasoning gives the clue to the absence of a band from the spectrum of ethyl crotonate itself:



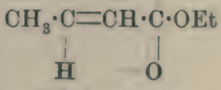
$$\begin{array}{l}CH_3\cdot C{=\!=}CH\cdot C\cdot OEt\\ \quad\ \ NH_2\ \cdots\cdots O\end{array}$$

Ethyl aminocrotonate.



$$\begin{array}{l}CH_3\cdot C{=}CH\cdot C\cdot OEt\\ \qquad\ Cl\ \ \cdots O\end{array}$$

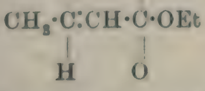
Ethyl chlorocrotonate.



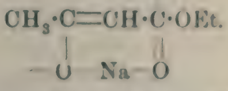
$$\begin{array}{l}CH_3\cdot C{=}CH\cdot C\cdot OEt\\ \qquad\ H\qquad O\end{array}$$

Ethyl crotonate.

Similar reasoning applies in the case of the enolic form of ethyl acetoacetate and its sodium derivative. In the enolic modification, since there is very slight ionisation, we are entitled to assume that the union between the hydrogen and oxygen atoms of the hydroxyl group is a strong one; but in the case of the sodium salt, which is much more readily dissociated, it must be assumed that this union is weaker. This would be represented in the two cases, as shown below, and it will be seen that the result in the one case is a more or less saturated hydrogen atom, whilst in the latter example there is an accumulation of free affinity on the sodium; so that the sodium salt gives results parallel with those obtained from ethyl aminocrotonate:



$$\begin{array}{l}CH_3\cdot C\!:\!CH\cdot C\cdot OEt\\ \qquad\ H\qquad\ O\end{array}$$

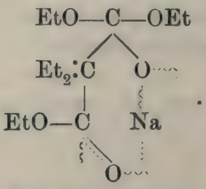


$$\begin{array}{l}CH_3\cdot C{=}CH\cdot C\cdot OEt.\\ \quad\ \cdots O\ \ Na\cdots O\end{array}$$

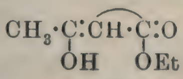
Thus we have a more or less clear expression of these differences, and the hypothesis appears to account for the salient facts, whilst it differs from Hantzsch's views only to the extent of the difference in interpretation of the state of affairs in the relations between the sodium atom and the carbonyl group.

One or two other points of interest have come to light in the course of this investigation. On examining the absorption spectrum of sodium malonate in alkaline solution, no band could be detected (see Fig. 2). This may be accounted for if we assume that the sodium derivative of sodium malonate is extremely easily hydrolysed by water.

On examining the spectrum of ethyl diethylmalonate (Fig. 3) we found that a considerable increase in the general absorption takes place on the addition of alkali to the solution. This might be accounted for by assuming some sort of space-conjugation between the carbonyl groups under the influence of the alkali, since these groups are in the critical 1:5-position with regard to one another. Or it might be explained by assuming the formation of an additive compound somewhat similar to those formulated by Gebhard (*loc. cit.*) in the case of the hydrochloride of benzopinacolin:

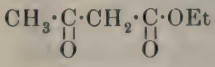


Turning to the action of hydrochloric acid on compounds containing a labile hydrogen atom, we have noticed a point which seems worth mentioning. Baly and Desch (*loc. cit.*) observed that the addition of hydrochloric acid rendered ethyl acetoacetate much more diactinic. On repeating this experiment with methyl malonate we found that the presence of hydrochloric acid made practically no difference to the spectrum of this substance. Now when the grouping (I), enolic form, is converted into (II), ketonic form, it will be seen that there is a decrease in the conjugation within the molecule; enolic ethyl acetoacetate contains two conjugated double bonds which are unconjugated in the ketonic substance:



$$\mathrm{CH_3\cdot\underset{OH}{C}:\overset{\frown}{CH}\cdot\underset{OEt}{C}:O}$$

(I.)

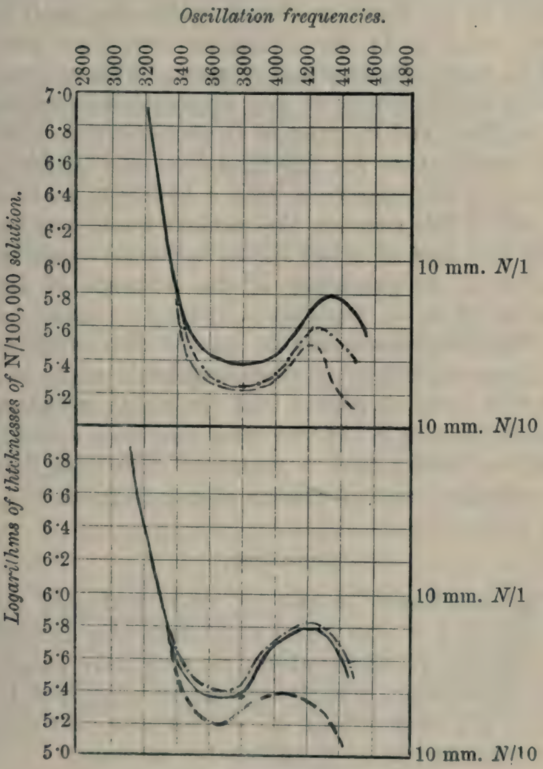


$$\mathrm{CH_3\cdot\underset{\underset{O}{\|}}{C}\cdot CH_2\cdot\underset{\underset{O}{\|}}{C}\cdot OEt}$$

(II.)

Hence it follows (Crymble, Stewart, Wright, and Glendinning, T., 1911, **99**, 451; Crymble, Stewart, Wright, and Miss Rea, *ibid.*, p. 1262) that the ketonic form will be the more diactinic of the two; and that the change from the enolic to the ketonic form will be accompanied by a decrease in absorptive power. Now K. H. Meyer (*Ber.*, 1912, **45**, 2846) has shown that ethyl acetoacetate in alcoholic solution contains 12·7 per cent. of the enolic form, which, being pseudo-acidic, will be converted into the ketonic form by the action of mineral acid. On the other hand, methyl malonate contains no enolic form under the same conditions, so that hydrochloric acid cannot have any influence in its case, which agrees with the spectroscopic results.

FIG. 4.



*Upper curves.*

——— *Acetone in water.*

— — — — — ,, ,, ,, + *N*-NaOH.

—·—·—·— ,, ,, ,, + *N*-HCl.

*Lower curves.*

——— *Acetone in alcohol.*

— — — — — ,, ,, ,, + *N*/10-NaOEt.

—·—·—·— ,, ,, ,, + *N*-HCl.

Finally, we come to a point which seems to be of some importance. It has been mentioned in the course of this paper that we tried the effect of adding alkali to a solution of mesityl oxide, but found that it produced no change in the substance's absorptive power. We have applied this test to several other substances, and have found that no marked change in their bands is produced by alkali. In the case of acetone * the amount of change produced either by acid or by alkali is almost within the limit of experimental error (see Fig. 4; the differences have been very slightly exaggerated to make the drawings clearer). This at once suggests that we have a test by which we may differentiate between different types of absorption, and we propose to continue this work immediately. It is possible that the differentiation may be found only in cases in which we are concerned with a hydrogen atom replacable by metals, and if this were so, the method would not be of much interest; but the case of ethyl diethylmalonate mentioned above seems to point to the possibility of the influence of alkali being traceable even when no replacable hydrogen atom is present. Hitherto it has been customary to assume that when two bands occurred at the same frequency, they owed their origin to analogous causes; but if it could be proved that the action of sodium or acid yielded different results in the two cases, this view would fall to the ground, and we should have a means of classifying bands much more accurately than any at present at our disposal.

## *Summary.*

(1) Various compounds containing labile hydrogen atoms have been examined, and it was found that these may be divided into two classes, namely, (i) those which, showing only general absorption in alcoholic solution, give rise to banded absorption in presence of alkali, and (ii) those which do not conform to this rule even when the sodium derivative is an isolable substance.

(2) In the case of those substance which develop a band in their spectrum in the presence of alkali it was shown that the persistence of the bands depends on the relative quantities of alkali present. This had already been shown by Hantzsch in the case of ethyl acetoacetate, and our work lends additional support to his view that the bands are merely the spectra of the alkali salts of these compounds containing the group $\cdot CO\cdot CH_2\cdot CO\cdot$.

(3) The alkali salt alone does not necessarily give rise to the band, but in those cases where the formation of internal complex

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* The curve for acetone in aqueous solution given in T., 1906, **87**, 492 seems to be incorrect. It was obtained with a spectrograph much inferior to the one now used by us and the error may be due to this cause (see Baly, T., 1910, **97**, 571 or a similar error in the case of nitrobenzene).

salts (or where there is a spatial possibility of mutual influence of free affinity) we have found a band in the spectrum; whereas in other cases where such conditions do not obtain we have not observed the production of any band.

(4) This work, which forms an extension of Hantzsch's, conclusively disproves the explanation put forward by Baly and Desch to account for these bands.

In conclusion, we desire to express our thanks to Professor Letts and Prof. Inglis for the interest they have taken in the work.

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## XLIX.—*The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures.*

By JOHN NORMAN COLLIE and HUBERT SUTTON PATTERSON.

THIS communication has been divided into two parts for the following reason. In the early portion of the work neither of the authors was aware of the work of the other, and it was not until the later stages that they had learnt that they were getting the same results independently; it seemed best therefore to collaborate and publish the work in a joint paper. Also, as both the authors had approached the problem from different points of view, it is better to keep the early results separate, in order to show how the two lines of research came together.

### PART I (BY J. N. COLLIE).

A good many years ago the author had noticed that many minerals change colour when bombarded by cathode rays, notably sodalite and fluorspar. At the same time much gas is given off. It was partly to investigate this change of colour, and partly to investigate the nature of the evolved gases, that from time to time various substances were subjected in tubes at low pressure to the action of high voltage electricity. In a letter to *Nature* last July (**89**, 502), Sir William Ramsay mentioned that the author had noticed that neon was present in the gas emitted from calcium fluoride when under the action of cathode rays. Both natural fluorspar, and calcium fluoride made by allowing hydrofluoric acid to act on lime, change colour when bombarded by cathode rays.

The substance becomes first pink, then purple, and in the case of crystals of fluorspar the surface becomes a deep purple, with a metallic, copper-coloured reflection. The action is only a surface one, and is probably due to metallic calcium, for if the purple substance is put into red litmus paper with some water the litmus becomes blue, and the purple compound disappears. The action of the cathode rays is therefore a powerful one, and if metallic calcium is set free, fluorine should be liberated as well. A small vacuum tube on the apparatus, however, gave no spectrum of fluorine, but only that of hydrogen and carbon gases. With the spark from a Leyden jar, silicon fluoride could be detected, and oxygen was also found in the gases, but this may have been formed by decomposition of water vapour.

It was found to be excessively difficult to get calcium fluoride in a condition so as to give no gas when bombarded by cathode rays. To give one experiment: Pure, fresh lime from marble was treated in a platinum basin with pure hydrofluoric acid in excess and evaporated to dryness. Again it was moistened with hydrofluoric acid, evaporated, and heated for a couple of hours in a muffle furnace to a temperature just short of fusion of the fluoride. As soon as cold it was put into a tube, in which it could be subjected to the cathode discharge. This tube had been carefully cleaned. After pumping out almost all the air from tube, the current was turned on, and gas at once began to come off the fluoride. By heating the fluoride with a bunsen burner, more gas came off, the gas being, as far as one could tell from the spectrum, a mixture of hydrogen and carbon monoxide. This evolution of gas from what was presumably pure calcium fluoride continued for about a week, the fluoride being bombarded by cathode rays and being heated for about six hours a day. During that time between 3 and 4 c.c. of gas were pumped off. Finally the tube ceased working, and no heating or bombardment by means of cathode rays liberated any more gas.

As this gas consisted almost entirely of carbon monoxide, hydrogen, oxygen, and a trace of silicon fluoride, these gases had presumably been formed from the calcium fluoride, water, and carbonaceous material in the tube; and the author has found that to get a tube that will not give carbon gases when it is violently heated and subjected at the same time to cathode discharge is a very difficult task.

The above mixture of gases were sparked, then treated with liquid air and charcoal, and the residue forced up into a capillary tube, where its spectrum could be obtained. This residue contained neon. This result being so extraordinary, further experiments were made. The length of the bombardment during the experiments was, as a rule, from three to six hours.

*Experiment* 1.—The calcium fluoride was replaced by some ten years old glass wool that had been carefully cleaned with sulphuric acid and chromic acid. The glass was dried at 120°. On bombarding with cathode rays, quantities of water vapour were evolved, and later carbon gases. These gases contained neon.

*Experiment* 2.—The glass wool was taken out of the tube, and in order that the current should pass at low pressures 3—4 c.c. of pure hydrogen were admitted little by little, and pumped off. The tube was heated during the experiment. The hydrogen was exploded with excess of pure oxygen, and the oxygen finally removed by charcoal cooled by liquid air. Neon was found.

It was then obvious that either the neon was being formed in the tube during the experiment, or that in some way air had leaked into the tube or the pump during the experiment. That air had not leaked into the pump was rendered highly improbable, for always at the end of a day's experiments a phosphorescent vacuum was left in the tube, and no change was found on examining the apparatus on the next day or the next but one. Moreover, a vacuum tube was in connexion with the tube, and the minutest trace of air would have meant a spectrum of nitrogen in the vacuum tube.

*Experiment* 3.—A tube was run intermittently for four days, and neon was found to be present. The oxygen gas that had been absorbed by the charcoal was collected, and put into a tube over mercury with phosphorus. All except a bubble the size of a large pin's head was absorbed. The amount of neon obtained in the experiment was about the same amount that was left when 1—2 c.c. of air were treated with cooled charcoal.* That would mean at least 1·0 c.c. of residual nitrogen if the neon found was due to an air leak. The pin's head of gas that remained over was found, however, when examined in a spectrum tube, to be pure hydrogen, and not nitrogen.

From time to time blank experiments were made with larger quantities of the oxygen † and hydrogen used; they were twice put through the pump in exactly the same way as during an experiment, and larger quantities than were used during an experiment were exploded and the residue tested. In no case was neon found.

*Experiment* 4.—A glass balloon was sealed on to the pump instead of the ordinary tube. This was exhausted and heated for two days to such a temperature that part of the bottom slightly collapsed. Some pure oxygen was then admitted to wash out any gas in the balloon. When tested for neon, none was found. This experiment shows that neon is not evolved from the glass by heating alone; moreover, glass heated to near its softening point is not a porous membrane to atmospheric neon or helium. Later a considerable amount of the same glass as that used during these experiments was pounded up, cleaned with chromic and sulphuric acids, and heated until it fused in a hard glass tube. The gas evolved was examined and contained no neon.

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* The neon obtained in all these experiments may have contained helium, but if the latter gas were present it was there in very small quantities. What was taken for the yellow helium line was only seen occasionally.

† The oxygen was prepared by heating potassium permanganate, and the hydrogen by the action of sodium amalgam on boiled water.

Experiments were also made to see whether the neon came from the aluminium electrodes that were always used.

A tube was made so that the negative electrode could be fused up in a small glass cup by means of an extra powerful discharge. This was done, and the gas evolved was examined. It contained hydrogen, for it could be exploded with oxygen, but the residue contained no neon. Later a much larger amount of the aluminium wire used in the experiments was fused by heating with a bunsen burner in a hard glass tube. Some hydrogen was evolved, but it did not contain neon.

There still remained a possibility, although glass was not porous to neon when heated (compare experiment 4), that it might be so when subjected to a cathode discharge.

*Experiment* 5.—A tube was made so that the end containing the negative electrode was surrounded by another that could be worked from a separate pump. Into the outer tube pure neon was admitted up to a pressure of half an atmosphere. After running the tube for six hours the gas in the inner tube contained neon as usual, and in about the same amount.

*Experiment* 6.—The neon was pumped out of the outer tube, and helium substituted instead; during four days' working the tube not a trace of helium could be found in the inner tube, but there was the usual amount of neon.

*Experiment* 7.—Another tube was then made so that the whole of the inner tube was contained in an outer one. After working it for two days with such a vacuum in the outer tube that the spark would not pass through it, and having hydrogen in the inner tube, the gases of the inner tube were examined, and found to contain the usual amount of neon. Merely for curiosity, a c.c. of oxygen was admitted into the outer tube and pumped out. It gave a very faint explosion (hydrogen) when a spark was passed through it in an eudiometer. The residual oxygen was then treated with cooled charcoal. The residue that remained was about fifty times as great as the residue from the inner tube, and when examined it was *mostly helium, with enough neon present to give the neon spectrum.*

Besides the above experiments many more were made, in all, thirty-five, and neon was found in greater or less quantity every time. Several times the lines were measured, and the following lines identified:

6678·50 6599·18 6506·69 6402·43
6383·14 6334·65 6163·73 6143·31
5096·36 6074·51 6030·20 5975·76
5882·06 5852·62

All the apparatus was made by the author, and all the electrodes were made from fresh aluminium wire, and had not been used for any other purpose.

## PART II (By H. S. PATTERSON).

This investigation was undertaken with the object of endeavouring to verify certain deductions from the formula for electronic mass:

$$m = \frac{2}{3}\,\frac{e^2}{a}.$$

$a$ = radius of electron supposed spherical.
$e$ = electric charge.
$m$ = mass.

If the chief part of the mass of an atom be supposed to be due to a similar cause to that of an electron, that is, if $m$ be the mass of an atom, $a$ the radius of the sphere which is the seat of the major part of the mass, and $e$ the charge on this sphere, then $a$ becomes very much smaller than the radius of an atom as measured by other methods. This does not cause difficulty, since the radius of an atom as measured directly depends on the nearness of approach of one atom to another, whilst $a$ is the radius of that part of the atom which is the seat of the major part of the mass. Suppose the $\alpha$-particle and the hydrogen ion be considered; then, since the electric charge on the $\alpha$-particle is twice that on the hydrogen ion, whilst their masses are in the ratio of 4 to 1, it follows that the radius of the seat of the major part of the mass of an atom may be the same in each case. If, therefore, by means of the electric discharge a second electric charge could be given to the seat of mass of the hydrogen ion, an $\alpha$-particle might be produced, in which case it would be possible to convert a hydrogen atom into one of helium.

One way of attempting to verify these deductions seemed to be to subject hydrogen at a low pressure to the electric discharge, and, after removing the excess of hydrogen, to examine the residue in a small spectrum tube.

The experiments were carried out in the following way. Hydrogen was prepared in an air-tight vessel by the electrolysis of a solution of barium hydroxide, boiled to free from air. The solution was purified from dissolved air finally, first by heating and passing through it about two litres of oxygen from a tube of potassium permanganate, which was then sealed off, and then by passing the current for some considerable time, when the solution became heated almost to boiling point, and allowing the electrolytic gas to escape. After these precautions, hydrogen, thus as completely as possible freed from air, was obtained on electrolysis, and after being dried over phosphoric oxide was let into a large Plücker tube with aluminium electrodes. The pressure in the discharge tube was at first about 2 mm., but was gradually reduced by an Antropoff pump to the point at which the discharge would only pass with great difficulty, the tube showing green phosphorescence. The process required in general about eight hours, the direction of the discharge being frequently reversed to get rid of any gas from the electrodes, and the discharge tube being continuously heated to obtain any gas driven into the glass. This was repeated until sufficient hydrogen, in some cases 30 c.c., had been treated. To the hydrogen which had been collected in an explosion tube was now added oxygen prepared from a potassium permanganate tube fixed on to the pump. After explosion of the hydrogen with excess of oxygen, the residue, consisting usually of about 0·1 c.c., and showing only the spectrum of oxygen, was taken into an apparatus in which the excess of oxygen could be removed by a charcoal bulb immersed in liquid air, whilst the gas remaining could be examined in a small spectrum tube. It was found that in fifteen experiments in which hydrogen was treated in this manner the spectrum of the final residue showed the presence of a quantity of neon. In four cases it was also possible to see faint traces of the spectrum of helium, but the spectrum of neon always very largely predominated.

To test the purity of the gases used, before each experiment a similar volume of hydrogen was treated in exactly the same way as before, but the discharge at low pressures was not passed. Under these conditions not the slightest trace of helium or neon could be detected. If even 200 c.c. of hydrogen were treated without passing the discharge, no helium or neon could be found. The oxygen was also treated in quantities both similar to and much greater than were used, by adsorption with charcoal cooled by liquid air, and examination for any residue. It was found, however, that not a trace of helium or neon could be seen. In all cases before an experiment the discharge tube was heated and exhausted until the discharge would only pass with great difficulty, and throughout the experiments the discharge tube was never open to the air. The aluminium of the electrodes was tested by melting in a vacuum, then washing out the tube with oxygen, and absorbing the oxygen by charcoal and examining the residue. Under these conditions not a trace of helium or neon was found.

With regard to the quantities of neon produced, it was found that from about 20 c.c. of hydrogen treated as above, the neon obtained was equivalent approximately to that occurring in 1 c.c. of air. The helium, however, was much less, for whilst in 1 c.c. of air the helium can be readily detected spectroscopically, in the experiments described the helium only occurred in such small quantities as to be almost invisible. It is noteworthy that on account of the adsorption of neon by charcoal, the tendency would be to increase the percentage of helium in the spectrum tube.

After hearing of Professor Collie's experiments with a jacketed cathode, experiments were made in double-walled discharge tubes. Hydrogen was put into the inner tube, in which were aluminium electrodes, and the experiment performed as before, the outer tube being exhausted so that the discharge would not pass. Under these conditions, neon, with a trace of helium, was found in the inner tube. Information having been received from Professor Collie that he had obtained large quantities of helium with some neon from the outer tube, this gas was looked for by washing out the outer tube with 1 c.c. of oxygen and absorbing the oxygen by charcoal cooled by liquid air. It was then found, in agreement with Professor Collie's results, that the residue consisted spectroscopically largely of helium mixed with a little neon. Another experiment was now made in which pure oxygen at a pressure of about 15 mm. was put into the outer tube, the inner tube containing hydrogen originally at a pressure of about 2 mm. On performing an experiment with the hydrogen in the inner tube as before, it was found that the residual gas in the inner tube consisted of neon. The major part of the oxygen in the outer tube was now removed by charcoal, the last 2 or 3 c.c. pumped out, and, after adsorption of the remaining oxygen, examined in a small spectrum tube. A residue was found which appeared spectroscopically to consist of almost pure neon with a little helium. In each of these last two experiments, the residue consisted of about a cu. mm. of gas, in the first case largely helium, in the second, largely neon.

### *Conclusion.*

Whatever the explanation of the above results may be, the facts seem to be the following:

1. Neon cannot be obtained from either the glass or the electrodes by heating alone.
2. The neon found is not due to air leaking into the pump or the apparatus during the experiment.
3. Glass, neither when heated to near its softening point, nor under the action of cathode rays, is permeable to ordinary neon or helium.
4. The hydrogen and the oxygen used in the experiments did not contain neon.

Moreover, the appearance of helium and neon in the outer tube as well as neon in the inner tube is most important. It would appear impossible that particles of these gases are shot through the glass from the inner to the outer tube; the question obviously is where do these gases come from? The answer to that question cannot at present be given with any certainty, but it is hoped that this line of research may ultimately throw more light on the subject. Since this paper was read Sir J. J. Thomson, in a letter to *Nature* (**90**, 645) gives an account of some experiments he has been making that have a direct bearing on the phenomena in question.

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## L.—*The Double Platinic and Cupric Iodides of Substituted Ammonium Bases.*

By RASIK LAL DATTA.

### *The Double Platinic Iodides.*

THE double platinic iodides of the alkali and alkaline earth metals were first prepared by Lassaigne (*Annalen*, 1833, **8**, 185) by dissolving platinic iodide in solutions of the respective metallic iodides. Later, Mather and Platt (*Amer. Chem. J.*, 1834, **27**, 257) prepared potassium platini-iodide by mixing a solution of platinic chloride with a slight excess of potassium iodide, evaporating to dryness on the water-bath, and extracting with a mixture of alcohol and ether so long as the colour was communicated to the washing liquid. It is evident that Mather and Platt obtained the compound in a highly impure state, largely contaminated with potassium chloride, since by this interaction much potassium chloride is formed which cannot entirely be washed out by the solvent used by them.

Kane (*Phil. Mag.*, 1833, **2**, 198) attempted to prepare ammonium and potassium platini-iodides by treating pulverised potassium iodide and ammonium iodide respectively with platinic chloride solution and washing the precipitates obtained with ether. His method, however, did not lead to the preparation of pure compounds, and he necessarily failed to arrive at a definite conclusion.

The following double iodides have been directly obtained as black, crystalline precipitates by adding platinic chloride to solutions of alkali and substituted ammonium iodides, but it has been found that double platinic iodides of sodium and alkaline earth metals could not be precipitated similarly owing to their extreme solubility.

### *Rubidium Platini-iodide.*

This salt is not so soluble as the potassium salt, as was to be expected from a comparison of the solubility of the platinichlorides. Hence it was obtained from a tolerably concentrated solution as a black, crystalline precipitate. It is moderately soluble in water:

0·3321 gave 0·4884 AgI. I=67·73.

$Rb_2PtI_6$ requires I=67·55 per cent.

### *Caesium Platini-iodide.*

This is a sparingly soluble salt, and was obtained by precipitation of dilute solutions:

0·1037 gave 0·1251 AgI. I=62·99.

$Cs_2PtI_6$ requires I=62·36 per cent.

It is a black powder, only sparingly soluble in water, forming a faintly-coloured solution. Its sparing solubility is quite in keeping with the intense electropositiveness of the metal, and it is one of the most stable platini-iodides.

### *Methylammonium Platini-iodide.*

This was obtained as a black precipitate, which was washed and dried in the desiccator over sulphuric acid:

0·2239 gave 0·0424 Pt. Pt=18·92.
0·1021 „ 0·1416 AgI. I=74·96.

$2CH_5N,H_2PtI_6$ requires Pt=19·09; I=74·63 per cent.

This salt is freely soluble in water, but less so than the corresponding salt with ammonium iodide, forming a deep red solution.

As a general rule it may be laid down that the solubility is dependent on the weight of the ammonium base, salts with the quaternary bases being the least soluble. This salt is sparingly soluble in a mixture of alcohol and ether, from which it may be crystallised.

### *Ethylammonium Platini-iodide.*

This compound is obtained as a crystalline, black precipitate soluble in water to a red solution. It was dried in the desiccator over sulphuric acid:

0·2132 gave 0·0400 Pt. Pt=18·76.
$2C_2H_7N,H_2PtI_6$ requires Pt=18·59 per cent.

### *Allylammonium Platini-iodide.*

To a concentrated solution of allylammonium iodide a 10 per cent. solution of platinic chloride was added; the solution became dark red, and in a few seconds a mass of slender crystals precipitated. These were collected, washed with a little water, and dried in the desiccator:

0·1044 gave 0·0189 Pt. Pt=18·10.
$2C_3H_7N,H_2PtI_6$ requires Pt=18·17 per cent.

### *Anilinium Platini-iodide.*

This is obtained as a black powder moderately soluble in water, giving a dark red solution:

0·2879 gave 0·0493 Pt. Pt=17·13.
$2C_6H_7N,H_2PtI_6$ requires Pt=17·06 per cent.

### *Dimethylammonium Platini-iodide.*

The compound is a black powder, soluble in water to a red solution. The solubility of this iodide is less than the primary ammonium platini-iodides:

0·2611 gave 0·0488 Pt. Pt=18·69.
0·1037 „ 0·1368 AgI. I=72·27.
$2C_2H_7N,H_2PtI_6$ requires Pt=18·59; I=72·64 per cent.

### *Diethylammonium Platini-iodide.*

The compound was obtained as a black precipitate:

0·2035 gave 0·0361 Pt. Pt=17·74.
$2C_4H_{11}N,H_2PtI_6$ requires Pt=17·64 per cent.

### *Trimethylammonium Platini-iodide.*

This compound is obtained as a black precipitate from moderately dilute solution:

0·2016 gave 0·0368 Pt. Pt=18·25.
0·0936 „ 0·1218 AgI. I=70·32.
$2C_3H_9N,H_2PtI_6$ requires Pt=18·10; I=70·75 per cent.

### *Triethylammonium Platini-iodide.*

This is a black powder, sparingly soluble in water:

0·2139 gave 0·0364 Pt. Pt=17·01.
$2C_6H_{15}N,H_2PtI_6$ requires Pt=16·88 per cent.

### *Tetramethylammonium Platini-iodide.*

Tetramethylammonium iodide is generally prepared by heating methyl iodide with alcoholic ammonia in a sealed tube. It was, however, obtained rapidly, and in a very short time by shaking in a stout, stoppered bottle a mixture of methyl iodide, aqueous ammonia, and methyl alcohol, the latter being added to facilitate the mixing of the iodide with aqueous ammonia. Heat was gradually developed, and a homogeneous mixture was obtained with the deposition of a fine, crystalline powder. By the time the bottle cooled, the deposition was complete. The crystals were washed with methyl alcohol and dried. The purity of the sample was ascertained by an iodine estimation. (Found, I=63·12. Calc., I=63·18 per cent.)

The double iodide was obtained as a black precipitate from moderately dilute solutions. It is sparingly soluble in water, giving a wine-red solution:

0·2677 gave 0·0472 Pt. Pt=17·62.
$2C_4H_{12}NI,PtI_4$ requires Pt=17·64 per cent.

### *Tetraethylammonium Platini-iodide.*

Unlike the compound just described, this has a red colour, and is very sparingly soluble in water:

0·2810 gave 0·0456 Pt. Pt=16·23.
$2C_8H_{20}NI,PtI_4$ requires Pt=16·02 per cent.

### *Pyridinium Platini-iodide.*

This compound is precipitated on adding platinic chloride to a dilute solution of pyridine hydriodide. The substance was obtained in an extremely fine state of division, and was difficult to wash.

The salt was dried as usual, and had a red tinge similar to that of the preceding compound. This red tinge may be characteristic of very heavily substituted ammonium bases, since it is absent in the case of the lower members:

0·2065 gave 0·0365 Pt. Pt=17·63.

$2C_5H_5N,H_2PtI_6$ requires Pt=17·47 per cent.

The reaction exemplified above may be used as a convenient analytical method for controlling the purity and composition of bases which are directly obtainable from reaction mixtures as iodides. Hitherto such iodides had to be converted into the chlorides through the hydroxides, and finally the platinichloride had to be prepared. It is, however, unnecessary to convert the iodide into its chloride, it being only requisite to add platinic chloride to the iodide solution direct, and to estimate platinum in the precipitated salt.

It may be pointed out that Peterson (*Zeitsch. anorg. Chem.*, 1898, **19**, 59), in describing the volumetric estimation of platinum, mentioned that platinic iodide is unstable, decomposing into platinous iodide and iodine. It is evident, however, from the isolation of platinic iodide itself by Lassaigne that Peterson's view as to the decomposability of platinic iodide is incorrect, and he was led to this conclusion by the fact that the reddish-brown solution can be titrated with thiosulphate. The titration becomes possible by the fact that sodium thiosulphate decomposes platinic iodide itself in combination with alkali and ammonium iodides.

### *The Double Cupric Iodides.*

By adding cupric chloride to solutions of the substituted ammonium iodides, a series of double salts with cupric iodide has been obtained. These double iodides are, however, highly unstable, and can only be prepared with difficulty, since they are readily decomposable by water into cuprous iodide, iodine, and the respective ammonium iodide. In this reaction the cupric iodide which is liberated in the presence of a large excess of substituted ammonium iodide finds a favourable opportunity of combining with the latter, and precipitates as an ammonium cupri-iodide. It is, in fact, the simultaneous combination with substituted ammonium iodides during the liberation of cupric iodide in the nascent state that makes the existence of these double cupric iodides possible, the ammonium iodides contributing materially to their formation by reason of their affinity towards iodine.

The formation of double cupric iodides with alkali metals and ammonia has been found to fail, the reaction taking the usual course. Iodides of ammonium bases which are heavily substituted, yield these double iodides with great facility. It is to be noticed that the more heavily the ammonium base is substituted the more stable is the double cupric iodide obtained with it. With those ammonium bases which are very lightly substituted, the double iodides could not be formed at all. With tolerably heavily substituted bases, the formation is somewhat difficult, and saturated solutions of the ammonium iodide must be used, since the double salt is decomposable by water, and might be precipitated in a decomposed state, mixed with free iodine; for instance, when a concentrated solution of cupric chloride is added to an excess of a saturated solution of tetraethylammonium iodide, a brick-red precipitate is obtained, which, when washed with water, decomposes, evidently owing to the decomposition of combined cupric iodide into cuprous iodide and iodine, which latter imparts a black colour to the precipitate. This behaviour is common to nearly all double iodides of this series, but there is a difference in the degree of decomposition depending on the weight of the base. In the same way, pyridinium iodide gives a salt which cannot be washed without turning black, and the salt with quinolinium iodide behaves similarly. It is interesting to note that these salts during their decomposition by water lose their crystalline shape, the whole congealing to a black, plastic mass. Tetrapropylammonium cupri-iodide has been found to be the most stable of all the double iodides that have been hitherto prepared, so much so that it can be washed freely with water, and remains undecomposed even when treated with large quantities of water.

It has to be noted that two series of salts have been obtained; for example, with tetraethylammonium iodide, as also with pyridinium or quinolinium iodide, salts of the type $2NR_4I, CuI_2$, or $(NR_4)_2CuI_4$ are formed; but with tetrapropylammonium iodide a salt of the type $NR_4I, CuI_2$, or $NR_4CuI_3$ is formed.

### *Tetraethylammonium Cupri-iodide.*

This was obtained as a brown precipitate by adding a concentrated solution of cupric chloride to a concentrated solution of tetraethylammonium iodide. It is important to note that during the washing of the salt the upper layer suddenly turns black, owing to the decomposition of the salt as mentioned above. However, the decomposition was avoided by using a small quantity of water:

0·2031 gave 0·0178 CuO. Cu = 7·00.

$2C_8H_{20}NI,CuI_2$ requires Cu = 7·58 per cent.

### *Tetrapropylammonium Cupri-iodide.*

This compound was obtained as a brick-red precipitate, which was washed with water, and dried in the desiccator. The salt is fairly stable, and can be washed freely without being decomposed. It has the formula $N(C_3H_7)_4I,CuI_2$:

0·2238 gave 0·0276 CuO. Cu = 9·86.
$C_{12}H_{28}NI,CuI_2$ requires Cu = 10·12 per cent.

### *Pyridinium Cupri-iodide.*

This salt was obtained by precipitating a concentrated solution of pyridine hydriodide by cupric chloride. It was collected by the aid of the pump so as to free it from the adhering mother liquor as far as practicable. The salt could not be washed, since the addition of only a small quantity of water has the effect of blackening, and hence decomposing the salt:

0·2512 gave 0·0249 CuO. Cu = 7·92.
$2C_5H_5N,2HI,CuI_2$ requires Cu = 8·62 per cent.

### *Quinolinium Cupri-iodide.*

This was obtained as a brick-red precipitate by the usual method. It cannot be washed for reasons previously indicated, and when added to a large volume of water, turns black, and its crystalline shape is lost, the whole congealing to a black, plastic mass:

0·2819 gave 0·0252 CuO. Cu = 7·14.
0·3215 ,, 0·0289 $Cu_2S$. Cu = 7·18.
$2C_9H_7N,2HI,CuI_2$ requires Cu = 7·58 per cent.

The low percentage of copper in the above salts is due to the impossibility of washing the salt free from the adhering ammonium iodides.

I take the opportunity to express my best thanks to Prof. P. C. Rây for his encouragement in carrying on the above investigation.

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## LI.—*The Absorption Spectra of Simple Aliphatic Substances in Solutions and as Vapours. Part II. Unsaturated Aldehydes and Ketones.*

By John Edward Purvis and Nial Patrick McCleland.

In a previous communication (T., 1912, **101**, 1810) the authors have given an account of the absorption spectra of various saturated aliphatic aldehydes and ketones in solutions, vapours, and thin films.

The aim of the present paper is to describe a series of observations of the absorption spectra in the ultra-violet regions of various unsaturated aldehydes and ketones when in solution and as vapours, and to compare them with several of their corresponding alcohol and acid derivatives.

The following substances were examined: acraldehyde, crotonaldehyde, citral, allylacetone, methyl allyl ketone, methyl propenyl ketone, mesityl oxide, phorone, allyl alcohol, allyl bromide, and crotonic acid.

The experimental methods have been described before. The substances were obtained by methods which are well known, with the exception, perhaps, of methyl allyl ketone, and this was prepared by the method described by Blaise (*Compt. rend.*, 1904, **138**, 284). We have to thank Mr. E. J. Holmyard for the specimen of citral.

### *Solutions.*

*Acraldehyde.*—The absorption curve of this substance in alcohol has been drawn (Fig. 1, I), from which it will be seen that there is one band the head of which is at about 1/λ 3150.

*Crotonaldehyde.*—The absorption curve (Fig. 1, II) shows one band at 1/λ 3130, which is weaker than that of acraldehyde.

*Citral.*—The absorption curve (Fig. 1, III) shows a very weak band at 1/λ 3030; and, on the more refrangible side, a still weaker one at 1/λ 4300, which, on the original photograph, appears more like a rapid extension of the rays between about λ 2500—λ 2280.

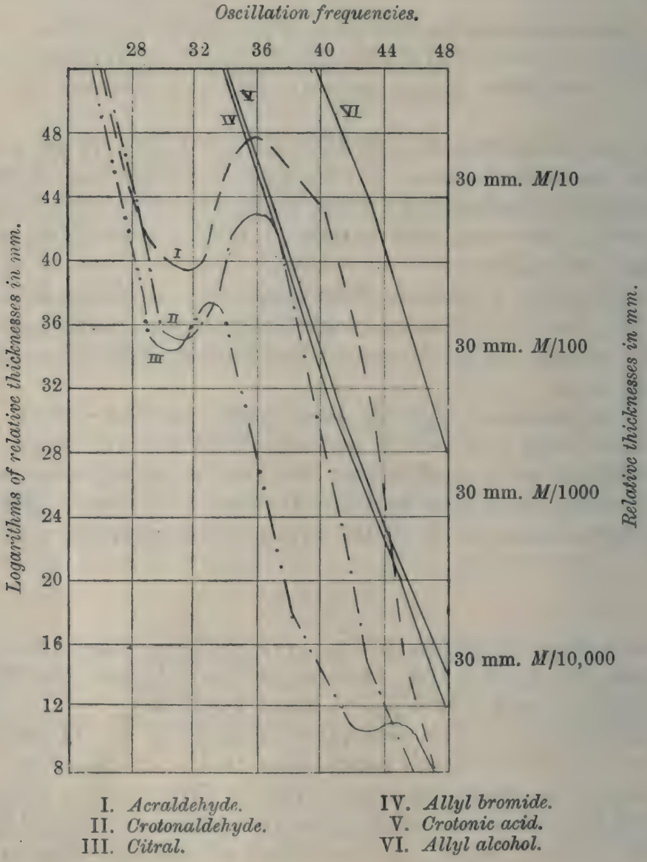
*Allylacetone.*—The absorption curve (Fig. 2, I) shows one band at 1/λ 3620.

*Methyl Allyl Ketone.*—The absorption curve of the substance in ether (Fig. 2, II) shows one hand at 1/λ 3450.

*Methyl Propenyl Ketone.*—The absorption curve of the substance in ether (Fig. 2, III) shows one band at 1/λ 3100. The band is very similar to that of methyl allyl ketone, and differs mainly in the position.

*Mesityl Oxide.*—The curve (Fig. 2, IV) shows a very weak band at about 1/λ 3200, which is weaker than the corresponding band of methyl allyl ketone and a second very weak band at 1/λ 4200, which on the photograph is more like a rapid extension of the rays between λ 2500—λ 2200, and it corresponds with the more refrangible band of phorone.

FIG. 1.

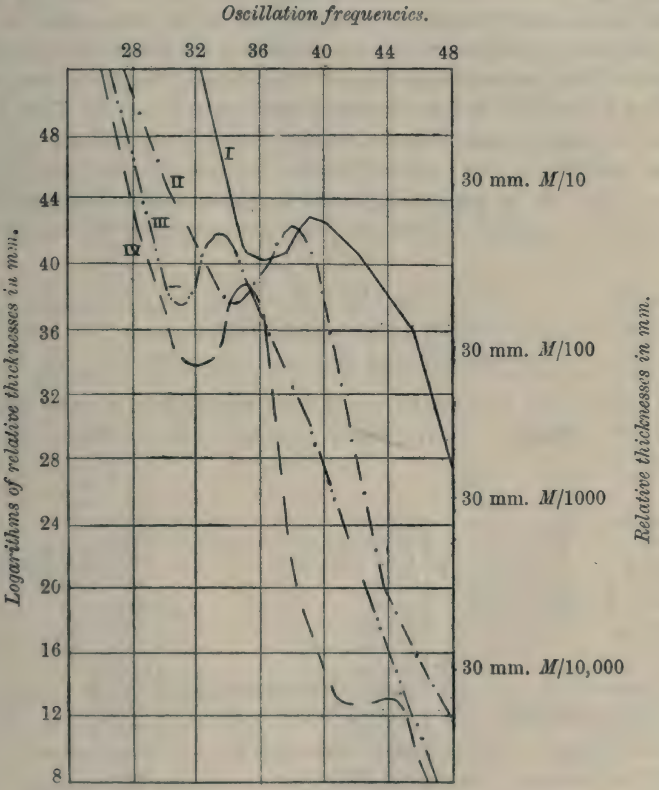


*Phorone.*—Baker and Baly (T., 1907, **91**, 1128) showed that the substance in solution had two bands, one at 1/λ 2850, and a stronger band at 1/λ 3730 in much weaker solutions. The authors have confirmed this observation.

*Allyl Alcohol.*—Hartley (T., 1881, **39**, 153), Drossbach (*Ber.*, 1902, **35**, 1486), and Magini (*Nuovo Cim.*, 1903, [v], **6**, 343) have shown that solutions of this substance had no bands. The authors have repeated the experiments, and have drawn the line of general absorption (Fig. 1, VI).

*Allyl Bromide.*—Ethereal solutions of this substance were also examined, but no bands were observed. The line of general absorption has been drawn (Fig. 1, IV).

FIG. 2.



I. *Allylacetone.* II. *Methyl allyl ketone.* III. *Methyl propenyl ketone.* IV. *Mesityl oxide.*

*Crotonic Acid.*—Solutions of this substance showed no band at any dilution. The line of general absorption has been drawn (Fig. 1, V). Stewart (T., 1907, **91**, 203) had also obtained a similar result.

*Results of the Examination of the Solutions.*—The results of the investigation of the absorption of the solutions are that the aldehydes and the ketones alone show specific absorption bands, the lighter substances having one band, and the heavier mesityl oxide, phorone, and citral showing two bands.

### *Vapours.*

*Acraldehyde.*—The absorption by the vapour of this substance may be described as a broad band, the less refrangible edge of which is broken up into a series of finer bands. The following table contains the measurements of the more refrangible edges of these narrow bands observed in the vapour, in a 200 mm. tube at 22° and 253 mm. pressure, using an acetylene light as the source of radiation. The vapour was also investigated at temperatures varying from 17° to 90°, and at increased pressures, the chief effect being that the weaker bands became stronger and more diffuse, and the general absorption was gradually extended towards the less refrangible regions. It is proposed to study these bands later with an instrument of greater dispersion than was available at the time.

### TABLE A.

*The Absorption Bands of Acraldehyde Vapour in a 200 mm. Tube at 22° and 253 mm. Pressure.*

*Abbreviations:* w. = weak; v.w. = very weak; mod.w. = moderately weak; str. = strong; f.str. = fairly strong; diff. = diffuse; narr. = narrow.

| | λ. | |
|---|---|---|
| | 4080 | v.w. |
| | 4040 | w. |
| | 4025 | w. |
| | 4010 | v.w. |
| | 3975 | v.w., diff. |
| | 3930 | ,, ,, |
| | 3895 | w. |
| | 3890 | v.w., narr. |
| | 3870 | v.w. |
| A | 3850 | str., mod. wide |
| | 3830 | f.str. ,, |
| | 3820 | w., narr. |
| | 3810 | ,, ,, |
| | 3800 | ,, ,, |
| | 3790 | ,, ,, |
| A′ | 3775 | str. |
| | 3765 | w., narr. |
| | 3755 | v.w., narr. |
| | 3740 | ,, ,, |
| | 3730 | ,, ,, |
| | 3710 | w. |
| | 3700 | w., diff. |
| | 3695 | w. |
| | 3685 | mod. str. & wide |
| | 3680—3660 | mod. str. & wide |
| | 3655—3650 | mod. str. & wide |
| | 3640 | mod. w. |
| | 3630 | ,, |
| | 3625 | ,, |
| | 3620 | ,, |
| | 3618 | ,, |
| | 3615 | ,, |
| | 3610 | v.w. |
| | 3600 | ,, |
| | 3590—3585 | mod. wide |
| | 3580 | mod. w. |
| | 3570 | ,, |
| | 3565 | ,, |
| | 3560 | ,, |
| | 3555 | w. |
| | 3550 | w. |
| | 3540 | w. |
| | 3535 | w. |
| | 3520 | mod. w. |
| | 3515 | v.w. |
| | 3510—3490 | w. |
| | 3486—3475 | v.w. |
| | 3465 | v.w. |
| | 3460 | ,, |
| | 3450 | ,, |

At about λ 3440 a broad band begins; and, using the cadmium spark as the source of light, a photograph showed that it extended, at 22° and 750 mm., to about λ 3060, and was diffuse on the more refrangible edge. Beyond this, the rays were transmitted to about λ 2270, where general absorption began.

There are several groups of the bands which are quite comparable in their general appearance, and amongst those the two groups *A* and *A'* are unmistakable. Also, there are several series of doublets and triplets representing bands of very similar appearance.

*Crotonaldehyde.*—The absorption by the vapour of this substance may, like that of acraldehyde, be described as a broad band, the less refrangible edge of which is broken up into a series of weak, narrow bands. The following table contains the measurements of the more refrangible edges of the finer bands observed in a 200 mm. tube at 16° and 751 mm. pressure, using an acetylene light as a source of radiation. The vapour was also examined at temperatures ranging from 16° to 90° and at increased pressures, the chief effect being that the weaker bands became stronger and more diffuse, and some of them widened into each other, whilst the general absorption extended more towards the less refrangible regions.

### TABLE B.

*The Absorption Bands of Crotonaldehyde Vapour in a 200 mm. Tube at* 16° *and* 751 *mm. Pressure.*

*Abbreviations:* w. = weak; v.w. = very weak; mod.w. = moderately weak; mod.str. = moderately strong.

| λ. | | λ. | |
|---|---|---|---|
| 3955 | w. | 3640 | v.w. |
| 3785 | v. w. | 3635 | ,, |
| 3775 | ,, | 3600 | ,, |
| 3760 | mod. str. | 3590 | ,, |
| 3730 | v.w. | 3570 | mod. w. |
| 3720 | ,, | 3560 | v.w. |
| 3700 | ,, | 3550 | ,, |
| 3690 | mod. w. | 3540 | ,, |
| 3675 | v.w. | | |
| 3670 | ,, | | |

On the more refrangible side of λ 3540 there are also several very weak finer bands, but they are too faint to measure them with any degree of accuracy. The broad band on the more refrangible side of the narrow bands expands and covers over some of the finer bands at increased temperatures and pressures. The position of the broad band, using the copper spark as the source of light, may be described as follows:

| t°. | Pressure in mm. | |
|---|---|---|
| 60 | 851 | The rays were absorbed between λ 3500—λ 3050 and then transmitted to λ 2470, when general absorption began. |
| 75 | 881 | The rays were absorbed between λ 3650—λ 2910 and then transmitted to λ 2510, when general absorption began. |
| 90 | 911 | The rays were absorbed between λ 3700—λ 2830 and then transmitted to λ 2600, when general absorption began. |

The bands are not so strong as those of acraldehyde; they are fewer in number, and they appear to consist mainly of doublets.

*Citral.*—There was considerable difficulty in the study of the vapour of this substance in consequence of its high boiling point and the weakness of the bands. When several drops of the liquid were placed in the 200 mm. absorption tube, the following phenomena were observed:

| t°. | Pressure in mm. | |
|---|---|---|
| 12 | 753 | The rays were transmitted to about λ 2230. |
| 30 | 797 | ,, ,, ,, λ 2270. |
| 45 | 823 | ,, ,, ,, λ 2400. |
| 60 | 853 | ,, ,, ,, λ 2480. |
| 75 | 883 | ,, ,, ,, λ 2550, and there were traces of a weakening between λ 3300—λ 3050. |
| 90 | 913 | The rays were transmitted to about λ 2650, and there was a more marked weakening between λ 3300—λ 3030. |

That is to say, between 30° and 45° there was a rapid absorption of the rays on the more refrangible side between λ 2400—λ 2270, denoting a very weak band, and comparable with a very weak solution band on the more refrangible side, and also traces of a very weak band on the less refrangible side between λ 3300—λ 3030 and comparable with the corresponding solution band. There were no traces of a resolution into a series of finer bands.

### *Allylacetone.*

| t°. | Pressure in mm. | |
|---|---|---|
| 15 | 759 | The rays were transmitted to λ 2120. |
| 30 | 803 | ,, ,, ,, ,, λ 2130. |
| 45 | 829 | ,, ,, ,, ,, λ 2140. |
| 60 | 859 | ,, ,, ,, ,, λ 2150; but they were weak between λ 2950—λ 2620. |
| 75 | 889 | The rays were transmitted to λ 2960; they were then absorbed to about λ 2530, and then transmitted to λ 2170. |
| 90 | 919 | The rays were absorbed between λ 3070—λ 2330, although the Cd lines 2748 and 2573 were feebly visible, and the series of Cd lines λ 2329 to λ 2265 were strong. |

That is to say, the vapour of allylacetone has one band comparable with the solution band, and it is not resolved into a series of finer bands.

### *Methyl Allyl Ketone.*

| t°. | Pressure in mm. | |
|---|---|---|
| 13 | 747 | The rays were transmitted to about λ 2360. |
| 30 | 781 | ,, ,, ,, λ 2400, but they were weak between about λ 3000—λ 2750. |
| 45 | 817 | The rays were absorbed between λ 3050—λ 2700 and then transmitted to λ 2440. |

| t°. | Pressure in mm. | |
|---|---|---|
| 60 | 847 | The rays were absorbed between λ 3100—λ 2650 and then transmitted to λ 2480. |
| 75 | 877 | The rays were transmitted to λ 3260; the Cd line 2573 was just visible. |
| 90 | 923 | The rays were transmitted to λ 3400. |

The observations show that the vapour of methyl allyl ketone has one band comparable with the solution band, and that it is not resolved into a series of finer bands.

### *Methyl Propenyl Ketone.*

| t°. | Pressure in mm. | |
|---|---|---|
| 12 | 741 | The rays were transmitted to λ 2410. |
| 30 | 785 | ,, ,, ,, λ 2470, but there was a little weakening between about λ 3300—λ 3060. |
| 45 | 811 | The rays were transmitted to λ 2590, but there was a definite weakening between about λ 3400—λ 3020. |
| 60 | 841 | The rays were absorbed between about λ 3500—λ 3000 and then transmitted to λ 2740. |
| 75 | 871 | The rays were transmitted to about λ 3570, but the Cd lines 3466, 2980, 2880, 2748 were just visible. |
| 90 | 901 | The rays were transmitted to 3620. |

These observations show that the vapour of methyl propenyl ketone has one band comparable with the solution band, and that it is not resolved into finer bands.

### *Mesityl Oxide.*

| t°. | Pressure in mm. | |
|---|---|---|
| 16 | 747 | The rays were transmitted to λ 2510. |
| 30 | 791 | ,, ,, ,, λ 2560. |
| 45 | 817 | ,, ,, ,, λ 2610, but they were weak between λ 3450—3020. |
| 60 | 847 | The rays were absorbed between λ 3600—λ 2890 and then transmitted to λ 2640. |
| 75 | 877 | The rays were absorbed between λ 3650—λ 2820 and then transmitted to λ 2670. |
| 90 | 907 | The rays were absorbed between λ 3710—λ 2770 and then transmitted to λ 2690. |

Experiments were conducted at 12° and 740 mm. pressure when the absorption tube contained a very small quantity of the vapour of mesityl oxide, in order to see if there were any traces of a more refrangible band comparable with that of the solution. It was noticed that the rays were transmitted to about λ 2370; there was weak absorption to about λ 2300, and then complete absorption beyond. This is comparable with the more refrangible solution band. So that there were two vapour bands, which were not resolved into finer bands. The continuous spectrum of an acetylene lamp was also used to investigate the less refrangible band, but no fine bands were observed.

### *Phorone.*

| t°. | Pressure in mm. | |
|---|---|---|
| 15 | 745 | The rays were transmitted to λ 2480; they became weak up to about λ 2250, and then feebly transmitted to λ 2130. |
| 20 | 775 | The rays were transmitted to λ 2550; they were absorbed to about λ 2330, and then feebly transmitted to about λ 2170. |
| 30 | 789 | The rays were transmitted to λ 2660. |
| 45 | 815 | ,, ,, ,, λ 2710. |
| 60 | 845 | ,, ,, ,, λ 2740. |
| 75 | 875 | ,, ,, ,, λ 2780, but they were weak between λ 3900—λ 3450. |
| 90 | 905 | The rays were transmitted to λ 4000; they were absorbed from λ 4000—λ 3350, and then transmitted to λ 2810. |
| 100 | 921 | The rays were absorbed between λ 4010—λ 3320, and then transmitted to λ 2850. |

That is to say, there were two bands comparable with the solution bands; but there was no resolution of these bands into a series of fine bands, similar to those observed in acraldehyde and crotonaldehyde. The continuous spectrum of an acetylene lamp was also used to investigate the less refrangible band, but no fine bands were observed.

### *Allyl Alcohol.*

| t°. | Pressure in mm. | |
|---|---|---|
| 30 | 808 | The rays were transmitted to λ 2100. |
| 45 | 834 | ,, ,, ,, ,, λ 2200. |
| 60 | 864 | ,, ,, ,, ,, λ 2270. |
| 75 | 894 | ,, ,, ,, ,, λ 2500; the series of Cd lines λ 2329—λ 2265 were visible. |
| 90 | 924 | The rays were transmitted to λ 2630. |

The light of an acetylene lamp was also used to investigate the less refrangible regions to about λ 2800, but no bands were observed.

### *Allyl Bromide.*

| t°. | Pressure in mm. | |
|---|---|---|
| 15 | 764 | The rays were transmitted to λ 2590. |
| 30 | 808 | ,, ,, ,, ,, λ 2670. |
| 45 | 834 | ,, ,, ,, ,, λ 2720. |
| 60 | 864 | ,, ,, ,, ,, λ 2760. |
| 75 | 894 | ,, ,, ,, ,, λ 2850. |
| 90 | 924 | ,, ,, ,, ,, λ 3140. |

That is to say, neither the vapours of allyl alcohol nor allyl bromide showed any trace of absorption bands. The whole of the bands found in acraldehyde have completely disappeared.

*Crotonic Acid.*

| t°. | Pressure in mm. | |
|---|---|---|
| 15 | 764 | The rays were transmitted to λ 2130. |
| 30 | 808 | ,, ,, ,, ,, λ 2150. |
| 45 | 834 | ,, ,, ,, ,, λ 2190. |
| 60 | 864 | ,, ,, ,, ,, λ 2230. |
| 75 | 894 | ,, ,, ,, ,, λ 2270, the series of Cd lines λ 2329—2265 were very weak. |
| 90 | 924 | The rays were transmitted to λ 2570; the Cd lines λ 2321 and λ 2313 were just visible. |

An acetylene lamp was also used for the less refrangible regions; but no band was observed. The experiments show that the vapour of crotonic acid has no band; the whole of the bands found in crotonaldehyde have completely disappeared.

*Results of the Examination of the Vapours.*—The results of the vapours are to show that only in acraldehyde and crotonaldehyde are there a series of fine bands on the less refrangible edges of a large strong band. None of these narrow bands occurs in the other ketones and aldehydes, which are characterised by wide bands comparable with the solution bands. Further, the corresponding alcohol, halogen derivative, and acid show no specific absorption, results which were similar in the solutions of these substances.

*Discussion of the Results.*—The more important results of this investigation are: (1) the considerable number of narrow bands found in the vapours of acraldehyde and crotonaldehyde, and which are absent from their solutions; (2) the absence of similar narrow bands from the vapours of other unsaturated aldehydes, ketones, alcohol, and acid; and the close similarity of their specific and general absorptions with those of the solutions.

If the absorption spectrum of acraldehyde is compared with that of propionaldehyde (*loc. cit.*), it will be noticed that the difference lies in a considerable shift of the band towards the less refrangible part of the spectrum, accompanied by its resolution into a series of narrow bands in the vapours. It is suggested that this is caused by the introduction of the ethenoid linking into the aldehyde, and that the change produces an effect comparable with that observed by the introduction of a second carbonyl group; and, further, that although all the atoms in a molecule are concerned in the final result, the fundamental influence originates in these primary oscillation centres. The results of this change were described by the authors in the first paper of this series (*loc. cit.*), and differ from those described above in the position of the less refrangible band, and in the fact that the more refrangible diffuse band of glyoxal and of dimethyl diketone is not observed in the spectrum of acraldehyde nor of crotonaldehyde, although it appears in the spectra of mesityl oxide, of citral, and of phorone.

Now the bands in glyoxal have been explained as the result of the interaction of two primary oscillation centres; and it was suggested that they are the consequence of electron vibrations governed by the laws expressed by the following equations *:

$$l\frac{d^2x}{dt^2} + m\frac{d^2y}{dt^2} + r\frac{dx}{dt} + cx = E \cos \mathrm{pt}.$$

$$m\frac{d^2x}{dt^2} + l\frac{d^2y}{dt^2} + r\frac{dy}{dt} + cy = E \cos \mathrm{pt}.$$

The authors propose to extend this explanation to the present case, on the assumption that an ethenoid linking also can function as a primary oscillation centre. A difficulty arises from the absence of direct observation of specific absorption in substances, such as ethylene, which have been found to be absolutely transparent within the limits available for ordinary observation in the ultraviolet. The possibility of selective absorption in the regions beyond 1/λ 5000 must not, however, be forgotten. The report of the Committee of the British Association (Portsmouth, 1911) on dynamic isomerism indicates the possibility of the head of a band at λ 1700 (1/λ 5800) in allyl alcohol, a region which is far beyond the reach of a photographic plate. It is, therefore, not improbable that the absorption shown by these substances originates in the hypothetical band of the ethenoid linking, strengthened and widened by the influence of the substituent.

If, then, it be assumed that the double bond is a primary oscillation centre, equations can be applied differing from the above only in the inequality of the coefficients in the two equations, since the two centres of absorption are no longer similar. The deductions from the equations are (1) that in acraldehyde and similarly constituted substances there will be two bands, namely, one, originating in the carbonyl group, in the less refrangible regions of the spectrum; and the other, originating in the ethenoid linking, in the region of very short wave-lengths; and (2) that the less refrangible band will show a tendency to break up into a series of fine bands or lines. The second of the two bands is, in the lower members of the series, outside the region ordinarily examined; but it appears on weighting the molecule in the neighbourhood of the ethenoid double bond, as in mesityl oxide, citral, and phorone. In the latter substances there are two ethenoid linkings, but the interaction between them is likely to be negligible, even in the case of phorone, since they are not adjacent. They will, therefore,

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* These equations were misprinted in the original paper.

merely reinforce one another in their action on the carbonyl group. This may explain the colour of phorone, where the band is displaced sufficiently into the visible spectrum for the colour to be noticed. In citral, however, the second double bond appears altogether too remote to produce any effect as regards colour, although the curving of the carbon chain might be thought to bring it into close proximity with the carbonyl group. In methyl allyl ketone and in allylacetone, where the two originating oscillation centres are separated by one and two methylene groups respectively, the phenomena observed are those indicated by the above hypothesis, the influence of the oscillation centres on one another falling off rapidly as their distance apart increases.

It will be noticed that, whereas the less refrangible bands of the vapours of acraldehyde and crotonaldehyde readily resolve themselves into fine bands or lines (the former more readily than the latter), the higher members of the series do not show these phenomena. This effect has been noticed in other substances, as, for example, in the benzene series (Hartley, *Phil. Trans.*, 1908, *A*, **208**, 475), the pyridine series (Purvis, T., 1910, **97**, 692), and by the authors in the aldehydes (*loc. cit.*). It seems to bear the interpretation of a general statement, namely, that, in a homologous series, as the molecular weight increases, the narrow vapour bands tend to coalesce into a single broad band.

We venture to think that the theory may be applied to explain the colour of the quinones; for the internal vibrations of each of the carbonyl groups will be influenced by those of the two adjacent ethenoid linkings, and, in addition, by those of the other carbonyl group. Sufficient thrust is, therefore, developed on the band originating in this group so that colour is the result. When either the carbonyl groups are removed, as in quinol, or the double bonds saturated, as in *cyclo*hexane-1:4-dione, the colour is destroyed, although there is still specific absorption in the ultraviolet. The colour of the fulgides may be explained on the same lines.

It will be noticed that this suggestion is very similar to Armstrong's theory in that colour is supposed to be caused by the presence of at least three unsaturated groups in the molecule. The authors, however, think that their suggestion covers more of the observed phenomena. It explains, for example, the colour of dimethyl diketone and kindred substances, and it is unaffected by the absence of colour in imino-*p*-benzoquinone.

It should be added that the great influence of the carbonyl group in the production of colour has previously been discussed by one of us (Purvis, T., 1910, **97**, 2535; 1911, **99**, 107), but at that time there was not sufficient material for a more extensive development of the subject; and in the case of none of these substances was it possible to study the vapour.

The authors are continuing the investigations with unsaturated hydrocarbons and other substances, and they desire to thank the Government Grant Committee of the Royal Society, by whose assistance some portion of the cost of the research was defrayed.

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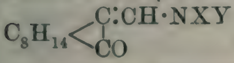
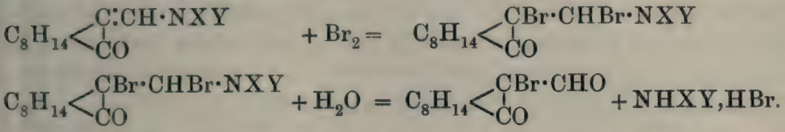
# LII.—*A Novel Method for Resolving Externally Compensated Amines*: *Derivatives of* d- *and* l-*Oxymethylenecamphor.*

By WILLIAM JACKSON POPE and JOHN READ.

EXTERNALLY compensated amines are usually resolved into their optically active components by crystallisation with an optically active acid in the manner suggested and applied by Pasteur; although the applications of this method of resolution have been greatly extended by the use of the optically active camphorsulphonic acids, as introduced by Pope and Peachey (T., 1898, **73**, 893), it quite frequently proves unavailing, owing either to the formation of partly racemic compounds or to unfavourable solubility relations between the two salts, *dAdB* and *dAlB*, produced. A method for resolving externally compensated primary amines, which embodied a new and useful idea, was devised by E. Erlenmeyer, jun. (*Ber.*, 1903, **36**, 976; *Annalen*, 1904, **337**, 307); this consists in condensing the amine with the aldehyde *d*-helicin and separating the *d*-helicin derivatives formed from the *d*- and the *l*-base by fractional crystallisation. Although the base is readily recovered from the condensation products by an easy hydrolysis, it is not to be anticipated that the method will prove of very general applicability; since the condensation products are glucosides their crystallisation may be expected to give difficulty. As is well known, other methods similar in character have been employed, but none have hitherto found extensive application.

We have previously shown that the condensation products formed from *d*-oxymethylenecamphor and a primary or secondary externally compensated amine can be used for the purpose of ascertaining whether the amine used is externally compensated or potentially optically inactive (T., 1909, **95**, 171); in the former case two condensation products are obtained, one containing the residue of the *d*- and the other of the *l*-base, whilst if the amine is potentially optically inactive only one acidic amide results. More recently we have shown (T., 1912, **101**, 2337) that the condensation product,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NXY\\ \,|\\ CO\end{array}$, is decomposed quantitatively, by titration in alcoholic solution with bromine, yielding bromo-oxymethylenecamphor and the hydrobromide of the amine, in accordance with the following equations:



$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot NXY\\ \,|\\ CO\end{array} + Br_2 = C_8H_{14}<\begin{array}{l}CBr\cdot CHBr\cdot NXY\\ \,|\\ CO\end{array}$$

$$C_8H_{14}<\begin{array}{l}CBr\cdot CHBr\cdot NXY\\ \,|\\ CO\end{array} + H_2O = C_8H_{14}<\begin{array}{l}CBr\cdot CHO\\ \,|\\ CO\end{array} + NHXY,HBr.$$

These equations are very similar to those given by Aschan and Brühl (*Ber.*, 1894, **27**, 2400) as representing the formation of bromo-oxymethylenecamphor and alkyl bromide by the action of bromine and water on the alkyl esters of oxymethylenecamphor.

### d- *and* l-*Oxymethylenecamphor.*

These substances were prepared from *d*- and *l*-camphor by Bishop, Claisen, and Sinclair's method (*Annalen*, 1894, **281**, 331); the previously unknown l-*oxymethylenecamphor* exhibits properties corresponding with those of its *d*-isomeride. The rotation constants and rotatory dispersions were determined with specimens which had been recrystallised from petroleum and left in a vacuum desiccator for two days; all the rotatory-power measurements given in the present paper were made, unless otherwise stated, on solutions prepared by making up the weight of material stated to 30 c.c. with the solvent, and examining the solution in a 4-dcm. tube at 20°.

*Solvent: Ethyl Alcohol.*

| | d-*Oxymethylenecamphor.* | | | l-*Oxymethylenecamphor.* | | |
|---|---|---|---|---|---|---|
| | 0·3027 gram. Time, 30 minutes. | | | 0·3023 gram. Time, 30 minutes. | | |
| | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. |
| α ... . ... | +9·77° | +8·44° | +7·98° | −9·65° | −8·35° | −7·87° |
| [α] ...... | +242 | +209 | +198 | −239 | −207 | −195 |
| [M] ...... | +436 | +376 | +356 | −431 | −373 | −352 |
| Rotatory dispersions: | 1·224; 1·058. | | | 1·226; 1·061. | | |
| | Time, 20 hours. | | | Time, 20 hours. | | |
| α ...... ... | +9·21° | +7·99° | +7·54° | −9·11° | −7·90° | −7·44° |
| [α] ...... | +228 | +198 | +187 | −226 | −196 | −185 |
| [M] ...... | +411 | +356 | +336 | −407 | −353 | −332 |
| Rotatory dispersions: | 1·221; 1·060. | | | 1·224; 1·062. | | |

The rotatory dispersions stated in this and the following determinations are, first, that for $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}}$, and secondly, that for $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}}$. Although the compounds exhibit marked mutarotation and the extent and velocity of the mutarotation are known to be dependent on the quantity and nature of the impurity present, the above values agree well amongst themselves and with the values previously given for sodium light (T., 1909, **95**, 176).

*Externally compensated oxymethylenecamphor* was prepared by allowing a solution of equal weights of the two components in light petroleum to crystallise slowly; it is indistinguishable in appearance and ordinary properties from the active isomerides, and melts at the same temperature, namely, 80—81°. Like the latter substances it becomes pasty and yellow with lapse of time.

### d- *and* l-*Bromo-oxymethylenecamphor.*

Considerable quantities of the bromo-oxymethylenecamphors were obtained in the course of the present work, and, as no standard determinations of the rotation constants of these substances have been hitherto published, it is desirable to record the values. The following data refer to *d*-bromo-oxymethylenecamphor.

*Solvent: Ethyl Alcohol.*

| | 0·3564 gram. Time, 30 minutes. | | | 0·3564 gram. Time, two days. | | |
|---|---|---|---|---|---|---|
| | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. |
| $\alpha$ ...... | +4·07° | +3·63° | +3·48° | +3·94° | +3·53° | +3·40° |
| $[\alpha]$ ... | +85·7 | +76·4 | +73·2 | +82·9 | +74·3 | +71·6 |
| [M]... | +222 | +198 | +190 | +215 | +192 | +185 |

Rotatory dispersions: 1·170; 1·043. 1·159; 1·038.

| | *Solvent: Ethyl Alcohol.* | | | *Solvent: Benzene.* | | |
|---|---|---|---|---|---|---|
| | 1·0100 gram. Time, two days. | | | 0·2549 gram. Time, 30 minutes. | | |
| $\alpha$ ...... | +11·58° | +10·29° | +9·91° | +3·14° | +2·82° | +2·74° |
| $[\alpha]$ ... | +86·0 | +76·4 | +73·6 | +92·4 | +83·0 | +80·6 |
| [M]... | +223 | +198 | +191 | +239 | +215 | +209 |

Rotatory dispersions: 1·169; 1·038. 1·146; 1·029.

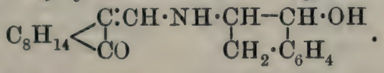
Although this substance shows little evidence of the occurrence of dynamic isomerism, behaving as if it had the true aldehydic constitution, it exhibits a slight but appreciable mutarotation in alcoholic solution; the rotation values become constant after two days. No mutarotation is to be observed in the benzene solutions.

l-*Bromo-oxymethylenecamphor* corresponds in properties with its enantiomorphously related isomeride.

### *Externally Compensated Bromo-oxymethylenecamphor.*

On crystallising equal quantities of the two optically active isomerides from alcohol the externally compensated substance is obtained in large, well-developed, almost square plates; it is less soluble than its components, forms much larger crystals, and exhibits no tendency to separate as an oil, as do the components. It melts at 46·5°, whilst the *d*- or *l*-isomeride melts at 44°. Both the active and externally compensated substances crystallise in nearly square plates, which show extinctions bisecting the angles, and probably belong to the orthorhombic system. After melting on a microscope slide, the three substances solidify to plates exhibiting slight double refraction; the modification thus first formed soon changes to a form identical with that deposited from solution. The close similarity in behaviour between the active and inactive isomerides suggests that the latter is not a racemic compound, although this is indicated by its sparing solubility.

### l-*Hydroxyhydrindamino*-d-*methylenecamphor*,



$$C_8H_{14}<\begin{matrix}C:CH\cdot NH\cdot CH-CH\cdot OH\\ CO\qquad\qquad CH_2\cdot C_6H_4\end{matrix}.$$

We have previously shown that externally compensated hydroxyhydrindamine can be very easily and completely resolved into its optically active components by crystallisation with *d*- and *l*-α-bromocamphor-π-sulphonic acid (T., 1912, **101**, 758). As a preliminary to effecting the resolution of the base by means of *d*-oxymethylenecamphor, the condensation products of the latter with the optically active amines were prepared.

The calculated quantity of *d*-oxymethylenecamphor dissolved in alcohol is added to a solution of *l*-hydroxyhydrindamine dissolved in 50 per cent. acetic acid, and the mixture warmed for a short time on the water-bath; dilute sodium hydroxide solution is then added, and the precipitated oil, which soon becomes semi-crystalline, washed with water and dissolved in warm alcohol. Water is added to the alcoholic solution in quantity just insufficient to produce turbidity, and the solution allowed to remain; l-*hydroxyhydrindamino*-d-*methylenecamphor* is then slowly deposited in colourless, six-sided, striated plates, which, after recrystallisation from aqueous alcohol, melt at 122°. The crystals obtained are complex interpenetration twins of a uniaxial material, and are extremely soluble in most of the usual organic solvents, with the exception of light petroleum:

0·0953 gave 0·2689 $CO_2$ and 0·0704 $H_2O$. C = 76·95; H = 8·27.

$C_{20}H_{25}O_2N$ requires C = 77·12; H = 8·10 per cent.

This substance exhibits very marked mutarotation in benzene, ethyl alcoholic, and glacial acetic acid solutions. A benzene solution containing 0·1552 gram in 30 c.c. gave the following values for $\alpha$: after 52 minutes, +0·58°; 92 minutes, +1·09°; 152 minutes, +1·76°; after 18 hours, +2·73°, and became constant after 48 hours with +2·71° for the mercury-green line. An ethyl-alcoholic solution containing 0·1490 gram in 30 c.c. similarly gave the following values of $\alpha$: after 30 minutes, +3·10°; after 1 hour, +3·13°; after 7 hours, +3·34°; and a constant value of +3·68° after 72 hours. A glacial acetic acid solution containing 0·0974 gram in 30 c.c. gave the value of $\alpha$ +2·01° after 1 hour, and a constant value of +1·66° after 18 hours.

After the rotatory powers of the above three solutions had become constant they were carefully determined, with the following results; these values may be therefore taken as the constants for the material:

| | Solution in benzene. | | | Solution in ethyl alcohol. | | |
|---|---|---|---|---|---|---|
| | $\mathrm{Hg}_{\text{green}}$. | $\mathrm{Hg}_{\text{yellow}}$. | $\mathrm{Na}_{\text{yellow}}$. | $\mathrm{Hg}_{\text{green}}$. | $\mathrm{Hg}_{\text{yellow}}$. | $\mathrm{Na}_{\text{yellow}}$. |
| $\alpha$ ……… | +2·71° | +2·21° | +2·05° | +3·68° | +3·12° | +2·89° |
| $[\alpha]$ …… | +131 | +107 | +99·1 | +185 | +157 | +145 |
| [M] …… | +407 | +333 | +308 | +575 | +488 | +451 |

Rotatory dispersions : 1·322 ; 1·078. 1·273 ; 1·080.

| | Solution in glacial acetic acid. | | |
|---|---|---|---|
| | $\mathrm{Hg}_{\text{green}}$. | $\mathrm{Hg}_{\text{yellow}}$. | $\mathrm{Na}_{\text{yellow}}$. |
| $\alpha$ ……… | +1·66° | +1·40° | +1·33° |
| $[\alpha]$ …… | +128 | +108 | +102 |
| [M] …… | +398 | +336 | +317 |

Rotatory dispersions : 1·248 ; 1·053.

Immediately after running bromine into an alcoholic solution of the substance until a faint, permanent yellow colour is obtained, the *hydrobromide* of the base separates in colourless, glistening needles; this salt is obtained in a pure condition by filtration and washing with acetone:

0·2440 required 10·6 c.c. $N/10$-$\mathrm{AgNO_3}$. Br = 34·72.

$\mathrm{C_9H_{11}ON,HBr}$ requires Br = 34·74 per cent.

0·1556 gram, in 30 c.c. of aqueous solution, gave, for the mercury-green line, $\alpha$ −0·66°, whence $[\alpha]$ −31·8° and [M] −73·2°.

As the molecular rotatory power of *l*-hydroxyhydrindamine hydrochloride for mercury-green light in aqueous solution is [M] −72·6° (T., 1912, **101**, 770), the hydrobromide now described is pure.

### d-*Hydroxyhydrindamino*-d-*methylenecamphor.*

This substance is prepared in a similar manner to the isomeride described above; it crystallises readily from aqueous alcohol in clusters of long, transparent needles, which soften at 115°, but only melt completely at 122°. It is the more soluble of the two isomerides:

0·1020 gave 0·2875 $CO_2$ and 0·0756 $H_2O$. C = 76·87; H = 8·29.
$C_{20}H_{25}O_2N$ requires C = 77·12; H = 8·10 per cent.

d-*Hydroxyhydrindamino*-d-*methylenecamphor* exhibits very marked mutarotation in benzene solutions: 0·1545 gram, made up to 30 c.c. with benzene, gave the following values of $\alpha$ for the mercury-green line: after 52 minutes, +9·09°; after 82 minutes, +9·00°; after 142 minutes, +7·73°; after 24 hours, +3·95°; after 54 hours the rotatory power became constant at $\alpha$ +3·92°. 0·1555 Gram, made up to 30 c.c. with ethyl alcohol, similarly gave the following values of $\alpha$: after 30 minutes, +9·83°; after 1 hour, +9·78°; after 7 hours, +9·23°; after 72 hours the rotatory power became constant with $\alpha$ +7·79°. The following determinations establish the rotation constants of the substances after equilibrium had become established in the two solutions just referred to:

| | In benzene, 0·1545 gram. | | | In ethyl alcohol, 0·1555 gram. | | |
|---|---|---|---|---|---|---|
| | Hg$_{\text{green}}$. | Hg$_{\text{yellow}}$. | Na$_{\text{yellow}}$. | Hg$_{\text{green}}$. | Hg$_{\text{yellow}}$. | Na$_{\text{yellow}}$. |
| $\alpha$ ........ | +3·92° | +3·37° | +3·16° | +7·79° | +6·61° | +6·27° |
| $[\alpha]$ ...... | +190 | +164 | +153 | +376 | +335 | +302 |
| [M] ...... | +592 | +509 | +477 | +1169 | +1042 | +939 |
| Rotatory dispersions: | 1·241 ; 1·066. | | | 1·242 ; 1·054. | | |

It is noteworthy that when the solutions of this substance in benzene and ethyl alcohol are examined immediately after being made up, the rotation constants are not greatly different in benzene and ethyl alcohol; the observed rotatory powers diminish rapidly in benzene solutions until, when constancy is attained, the specific rotatory powers for the several wave-lengths are just about one-half as great in benzene as in alcoholic solution. Both the condensation products described above are very stable in the presence of boiling concentrated hydrochloric acid or hot concentrated sodium hydroxide solution.

The d-*hydroxyhydrindamine hydrobromide* obtained by treating *d*-hydroxyhydrindamino-*d*-methylenecamphor with bromine and alcohol in the manner previously described was found to have the molecular rotatory power [M] +73·0° for the mercury-green line in dilute aqueous solution; it is thus evidently a pure substance.

### *Resolution of Externally Compensated Hydroxyhydrindamine.*

Externally compensated hydroxyhydrindamine hydrochloride is dissolved in 50 per cent. acetic acid and warmed with one molecular proportion of *d*-oxymethylenecamphor in alcoholic solution, the product being isolated as in the previously described cases. The aqueous alcoholic solution of the condensation product, when exposed in an open dish at the ordinary temperature, slowly deposits minute, glistening needles, melting at about 118°; further crops of the same crystalline material are successively deposited, mixed with a little oily matter, which is caused to redissolve by the addition of alcohol.

The crude, crystalline deposit thus obtained proved to be practically pure *l*-hydroxyhydrindamino-*d*-methylenecamphor; 0·1436 gram, made up to 30 c.c. with benzene, gave a constant value for the mercury-green line of $\alpha$ +2·54° after 30 hours' keeping; whence $[\alpha]$ +133°, the constant for the pure compound being $[\alpha]$ +131°. On recrystallisation from aqueous alcohol the characteristic, composite, six-sided plates of the substance are obtained; 0·1608 gram, made up to 30 c.c. with ethyl alcohol, gave a constant value of $\alpha$ +3·97° for the mercury-green line after 50 hours' keeping; the specific rotatory power is thus $[\alpha]$ +185°, a value identical with that for the pure substance stated above.

The separation of the *l*-component as its *d*-methylenecamphor derivative from the externally compensated amine can thus be effected very sharply indeed; as the isomeric *d*-hydroxyhydrindamino-*d*-methylenecamphor tends to separate as an oil, the isolation of the pure *d*-base is not conveniently attempted in the same operation. In accordance with previous experience it is, however, obviously possible to separate the latter isomeride with the aid of *l*-oxymethylenecamphor.

### l-*Hydroxyhydrindamine Hydrobromide.*

This salt is conveniently obtained in a pure, crystalline condition, as previously indicated, by the action of bromine and alcohol on *l*-hydroxyhydrindamino-*d*-methylenecamphor; it forms long, colourless, glistening needles, and is very soluble in water:

0·2245 required 9·7 c.c. *N*/10-$AgNO_3$. Br = 34·53.

$C_9H_{11}ON,HBr$ requires Br = 34·74 per cent.

The rotation constants of the salt in aqueous solution were determined for comparison with those of the hydrochloride (*loc. cit.*, p. 770).

| | Solvent: water, 0·1507. | | |
|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
| $\alpha$ | −0·64° | −0·55° | −0·53° |
| $[\alpha]$ | −31·9 | −27·4 | −26·4 |
| [M] | −73·3 | −63·0 | −60·7 |
| [M] for the pure hydrochloride | −72·6 | −63·4 | −61·1 |

### *Resolution of Externally Compensated α-Phenylethylamine.*

In a previous paper we have referred to the difficulty of resolving externally compensated α-phenylethylamine (T., 1909, **95**, 172), and have shown that on treatment with *d*-oxymethylenecamphor it yields two isomeric condensation products, which are very stable towards hydrolysing agents. The less soluble product melts at 145—148°, and was described in our previous paper as *d*-α-phenylethylamino-*d*-methylenecamphor; the results obtained from its decomposition now show it to be *l*-α-phenylethylamino-*d*-methylenecamphor. The more soluble condensation product melting at 112—114·5° is now proved to be somewhat impure *d*-α-phenylethylamino-*d*-methylenecamphor; the corrected names will be applied to the substances in the following pages.

*l*-α-Phenylethylamino-*d*-oxymethylenecamphor is readily separated in a pure state and in good yield from the product of treating the externally compensated amine with *d*-oxymethylenecamphor; its alcoholic solution readily decolorises bromine, but the hydrobromide of the base is not easily separated in a crystalline condition. The mixture of hydrobromide and *d*-bromo-oxymethylenecamphor obtained by the action of alcohol and bromine was therefore mixed with warm water and extracted with benzene; the aqueous solution of the hydrobromide was then treated with benzoyl chloride and sodium hydroxide, and benzoyl-*l*-α-phenylethylamine obtained. This substance separates from aqueous alcohol in fine, lustrous needles, melting at 119·5°, a lower value than that of 125·5° given by Marckwald and Meth (*Ber.*, 1905, **38**, 801); in a benzene solution containing 3·005 per cent. of the benzoyl derivative the latter workers obtained the specific rotatory power $[\alpha]_D$ −39·9°, whilst for the same concentration at 20° we obtained the nearly identical value of $[\alpha]_D$ −40·1°. This concentration represents a practically saturated solution. Marckwald and Meth showed that the specific rotatory power of this compound varies in a remarkable manner with the solvent, and we now find that the values in benzene solutions change considerably with the concentration; the following three sets of determinations refer to benzene solutions at 20°. Set I was made in 2-dcm. tubes on a solution containing 0·6008 gram in 20 c.c., the concentration being thus 3·004 per cent.; solutions II and III were examined in 4-dcm. tubes, and contained respectively 0·7152 gram and 0·2384 gram in 30 c.c., the concentrations being thus 2·3840 and 0·7947 per cent.

| | I. | | | II. | | |
|---|---|---|---|---|---|---|
| | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. |
| α ……… | −2·90° | −2·52° | −2·41° | −5·02° | −4·36° | −4·17° |
| [α] …… | −48·3 | −41·9 | −40·1 | −52·6 | −45·7 | −43·7 |
| [M] …… | −137 | −119 | −114 | −149 | −129 | −124 |
| Rotatory dispersions: | 1·203; 1·046. | | | 1·204; 1·046. | | |

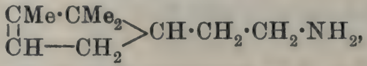
| | III. | | |
|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
| α ......... | −2·04° | −1·77° | −1·67° |
| [α] ...... | −64·2 | −55·7 | −52·5 |
| [M] ...... | −182 | −158 | −149 |

Rotatory dispersions: 1·222; 1·060.

The *d*-α-phenylethylamino-*d*-methylenecamphor melting at 112—114·5° after subjection to a series of operations similar to that described in connexion with its isomeride, yielded a benzoyl derivative, which separated from aqueous alcohol in soft, opaque, feathery needles, melting at 110—111°; a 2·7 per cent. benzene solution of the benzoyl derivative gave $[\alpha]_D$ +26·0°. By comparison with the data given above for the benzoyl derivative of the pure *l*-base it is seen that it contains only 80 to 85 per cent. of benzoyl-*d*-α-phenylethylamine. The method of resolving the externally compensated base now described is thus a very convenient one for the isolation of *l*-α-phenylethylamine and its derivatives, but cannot be economically applied to the preparation of the enantiomorphously related component; this latter could naturally be obtained by the use of *l*-oxymethylenecamphor.

### *Condensation of Oxymethylenecamphor with* d-α-*Camphylamine.*

The primary base, α-camphylamine,



$$\left.\begin{array}{l}\text{CMe}\cdot\text{CMe}_2\\ \text{CH}\text{—}\text{CH}_2\end{array}\right>\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2,$$

obtained by the reduction of α-campholenonitrile, has been but little studied; as it exhibits only a small rotatory power of $\alpha_D$ +6° in a 1-dcm. tube (Tiemann, *Ber.*, 1896, **29**, 3009) it might be expected to consist of a mixture of two enantiomorphously related isomerides. Our method of ascertaining whether an amine is potentially inactive or resolvable into stereoisomerides, with the aid of *d*-oxymethylenecamphor, can be conveniently applied to this base, and we have therefore examined its condensation products.

Our preparation of *d*-α-camphylamine boiled at 202—204° under one atmosphere pressure, instead of at 194—196° as stated by Tiemann; its density was $d$=0·8688 at 20°, and it gave the following results on examination in a 4-dcm. tube at 20°:

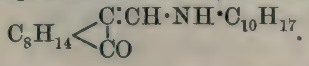
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
|---|---|---|---|
| α ............ | +14·62° | +13·61° | +13·30° |
| [α] ......... | +4·27 | +3·92 | +3·83 |
| [M] ......... | +6·53 | +6·00 | +5·86 |

Rotatory dispersions: 1·099; 1·023.

The rotatory power is thus smaller than that observed by

Tiemann, and it is further noteworthy that the rotatory dispersion for $Hg_{green}/Na_{yellow}$ has an unusually low value.

### d-*α-Camphylamino*-l-*methylenecamphor*,



$$C_8H_{14}<\begin{matrix}C{:}CH\cdot NH\cdot C_{10}H_{17}\\ |\\ CO\end{matrix}.$$

On mixing an alcoholic solution of *l*-oxymethylenecamphor with a solution of the base in dilute acetic acid the condensation product is immediately precipitated as an oil. After heating the mixture on the water-bath with the addition of sufficient alcohol to dissolve the oil, and allowing to cool slowly, a crystalline product separates; after collection and recrystallisation from warm acetone the compound is obtained in glistening, colourless needles, melting rather indefinitely at about 140°. On slow crystallisation from acetone it separates in long, well-developed, transparent prisms, which exhibit a fibrous cleavage, and slowly turn pink on exposure to the air:

0·1038 gave 0·3032 $CO_2$ and 0·0965 $H_2O$. C=79·66; H=10·40.

$C_{21}H_{33}ON$ requires C=79·93; H=10·55 per cent.

Since *α*-camphylamine is a primary amine it would be expected, in accordance with our previous results, that its *d*-methylenecamphor derivative would exhibit mutarotation in neutral solutions; the rotatory power of the alcoholic solutions does, indeed, change with lapse of time, although very slowly.

*Solvent: Ethyl Alcohol.*

| | 0·1065 gram. Time, 1 hour. | | | 0·5028 gram. Time, 1 hour. | | |
|---|---|---|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
| α ........ | −4·17° | −3·54° | −3·33° | −19·69° | −16·69° | −15·76° |
| [α] ...... | −294 | −249 | −235 | −294 | −249 | −235 |
| [M] ...... | −925 | −785 | −739 | −925 | −784 | −741 |
| Rotatory dispersions: | 1·252; 1·063. | | | 1·249; 1·059. | | |

The more dilute solution gave the following values of *α* for the mercury-green line: after 24 hours, −4·01°; after 72 hours, −3·91°; after 96 hours, −3·89°. The mutarotation, although slight, is therefore quite appreciable.

### d-*α-Camphylamino*-d-*methylenecamphor*.

This substance is obtained in the same way as the foregoing, but in the preparation great care must be taken to free the crude product from traces of the original amine and oxymethylenecamphor, because otherwise crystallisation cannot be induced. The crude product is therefore extracted with light petroleum, and the solution shaken several times with dilute sodium hydroxide, and subsequently with dilute hydrochloric acid; this treatment is repeated until crystalline material separates from the petroleum solution. The solid deposit is crystallised from warm acetone, and is then obtained in fine, glistening needles, melting at 155—158°. The pure compound is moderately soluble in warm acetone, but practically insoluble in light petroleum:

0·1045 gave 0·3066 $CO_2$ and 0·0970 $H_2O$. C=80·02; H=10·39.
$C_{21}H_{33}ON$ requires C=79·93; H=10·55 per cent.

The following determinations of rotatory power were made with an alcoholic solution containing 0·1000 gram in 30 c.c. one hour after solution:

| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
|---|---|---|---|
| α ......... | +3·31° | +2·78° | +2·63° |
| [α] ...... | +248 | +209 | +197 |
| [M] ...... | +782 | +657 | +621 |

Rotatory dispersions: 1·259; 1·057.

The observed rotatory power, α, for mercury-green light changed in the following manner with lapse of time: after 26 hours, +2·33°; after 42 hours, +2·02°; after 67 hours, +1·76°. The mutarotation is thus more rapid than in the case of the previously described isomeride; it is noteworthy that the rotatory dispersions of the two substances are nearly the same.

As in the preparation of these two stereoisomerides no evidence was obtained of the formation of other products, it seems justifiable to conclude that the original base is an optically pure substance, and that it may be described as *d*-α-camphylamine.

### *Condensation of* d-α-*Camphylamine with* dl-*Oxymethylenecamphor.*

The condensation of *d*-α-camphylamine with externally compensated oxymethylenecamphor occurs readily, and the product is caused to crystallise as described above. The resulting substance is, as is to be expected, a mixture of two stereoisomerides, but, owing apparently to the similar solubility of the isomerides and to the occurrence of tautomeric change, it was found impossible to effect a complete separation by fractional crystallisation. The specific rotatory power of the various fractions obtained varied between −66·4° and +5·0° in alcoholic solution for mercury-green light; no evidence was forthcoming in favour of the existence of a partly racemic compound which would have the specific rotatory power of [α] −23° for mercury-green light in alcoholic solution.

### *Separation of* d-*Bornylamine and* d-neo*Bornylamine.*

Considerable difficulties are frequently encountered in the attempt to separate the *cis*- and *trans*-isomerides of amines which contain several asymmetric carbon atoms in the molecule; in view of the ease with which the resolution of externally compensated amines can be effected by the aid of the oxymethylenecamphors, it appeared desirable to apply the method to some instance of the kind just mentioned. One of the most difficult separations of this nature seems to be presented by the reduction product of *d*-camphoroxime described by Forster (T., 1898, **73**, 391; 1900, **77**, 1152), and shown by him to consist of a mixture of the *cis*- and *trans*-isomerides distinguished as *d*-bornylamine and *d*-*neo*bornylamine; this mixture cannot be resolved by crystallisation with *d*-α-bromocamphor-π-sulphonic acid (Pope and Read, T., 1910, **97**, 987). Although the isolation of pure *d*-bornylamine from the mixture can be effected (compare Frankland, T., 1909, **95**, 2017) by fractionally crystallising the mixture of hydrochlorides, it presents considerable difficulties. Dr. Forster was so good as to provide us with several of his preparations, which represented mixtures of the hydrochlorides of *d*-bornylamine and *d*-*neo*bornylamine in different proportion, for use in the present work; the experimental study of the condensation products which these materials yield with the oxymethylenecamphors has enabled us to devise a comparatively simple method for the preparation of pure *d*-bornylamine.

### *Preparation of Pure* d-*Bornylamine and its Derivatives.*

A mixture of the hydrochlorides of the two isomeric bases, obtained during the working up of the reduction product of *d*-camphoroxime, was found to give the specific rotatory power for the mercury-green line in dilute aqueous solution of [α] +9·4°; the molecular rotatory power is thus [M] +17·8°, corresponding with a content of about 79 per cent. of *d*-bornylamine hydrochloride. The solution of this mixture in 50 per cent. acetic acid was treated with the corresponding quantity of *d*-oxymethylenecamphor in ethyl-alcoholic solution in the manner already described; on warming for a short time on the water-bath a crystalline product separates, and, after addition of dilute sodium hydroxide solution, this is collected and washed with dilute hydrochloric acid and water. In one experiment 0·1038 gram of the product, made up to 30 c.c. with ethyl alcohol, and examined at 20°, gave the specific rotatory power [α] +329° after 4 hours, rising after 48 hours to +345°, for the mercury-green line.

On allowing the concentrated solution in hot acetone of this crude product to remain, successive deposits of long, lustrous needles were obtained; the first five of these gave, for the mercury-green line, the specific rotatory powers, [α] +387°, +381°, +368°, +364°, and +287° half an hour after being made up in alcoholic solution. Most of the crystalline material was contained in the first two fractions, and the mother liquor remaining after the deposition of the fifth fraction contained an extremely soluble substance. As the result of a considerable amount of experimental work it was ascertained that the first fraction consisted of pure *d*-bornylamino-*d*-methylenecamphor, and that the remaining crystalline fractions yielded this substance in a pure state after one recrystallisation from aqueous alcohol. The specific rotatory power varies from [α] +390° to +450° for the mercury-green line in a freshly prepared 0·5 per cent. alcoholic solution, the precise value doubtless depending on the conditions attending crystallisation. The carefully purified substance forms long, colourless needles melting at 230°, and is moderately soluble in hot alcohol, but almost insoluble in acetone:

0·1151 gave 0·3368 $CO_2$ and 0·1105 $H_2O$. C=79·80; H=10·74.

$C_{21}H_{33}ON$ requires C=79·93; H=10·55 per cent.

An ethyl-alcoholic solution containing 0·1058 gram in 30 c.c., examined in a 4-dcm. tube at 20°, gave the specific rotatory power [α] +396° for the mercury-green line 30 minutes after having been made up; this value increased to +410° after 48 hours keeping, and was then constant. The standard determinations obtained after this interval are as follows:

*After* 48 *hours. Solvent: Ethyl Alcohol.* 0·1058 Gram.

| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
|---|---|---|---|
| α | +5·79° | +4·90° | +4·65° |
| [α] | +410 | +347 | +330 |
| [M] | +1292 | +1093 | +1039 |

Rotatory dispersions: 1·245; 1·054.

The warm alcoholic solution of this substance reacts immediately with bromine, and, after evaporating off the alcohol on the water-bath, the residue is freed from *d*-bromo-oxymethylenecamphor by extraction of its aqueous solution with benzene; the aqueous residue is evaporated to dryness, and the crude hydrobromide purified by recrystallisation from acetone or by precipitation from its alcoholic solution by the addition of ether.

### d-*Bornylamine Hydrobromide.*

In the process just above described this salt is obtained in thin, transparent, colourless prisms, which are extremely soluble in water or alcohol, and readily soluble in acetone; the yield is theoretical:

0·2016 required 8·6 c.c. $N/10$-$AgNO_3$. Br=34·09.

$C_{10}H_{19}N,HBr$ requires Br=34·14 per cent.

Since this compound is a pure salt of *d*-bornylamine it appeared desirable to make the following standard determinations of its rotation constants.

*Solvent: Water.*

| | 0·7396 gram in 30 c.c. | | | 0·3070 gram in 30 c.c. | | |
|---|---|---|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
| α ......... | +2·04° | +1·82° | +1·74° | +0·85° | +0·76° | +0·72° |
| [α] ...... | +20·7 | +18·5 | +17·6 | +20·8 | +18·6 | +17·6 |
| [M] ...... | +48·4 | +43·2 | +41·3 | +48·6 | +43·5 | +41·3 |

Rotatory dispersions: 1·172; 1·046. 1·181; 1·056.

*Solvent: Ethyl Alcohol.*

| | 1·4792 gram in 30 c.c. | | | 0·4931 gram in 30 c.c. | | |
|---|---|---|---|---|---|---|
| α ......... | +4·40° | +3·90° | +3·73° | +1·44° | +1·28° | +1·22° |
| [α] ...... | +22·3 | +19·8 | +18·9 | +21·9 | +19·5 | +18·6 |
| [M] ...... | +52·2 | +46·3 | +44·2 | +51·2 | +45·6 | +43·4 |

Rotatory dispersions: 1·180; 1·046. 1·180; 1·048.

*Solvent: Chloroform.*

| | 0·2018 gram in 30 c.c. | | |
|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
| α .................... | +0·86° | +0·72° | +0·70. |
| [α] .................... | +32·0 | +26·8 | +26·0 |
| [M] .................... | +74·8 | +62·6 | +60·9 |

Rotatory dispersions: 1·229; 1·029.

It is noteworthy that the rotation constants and the rotatory dispersions are nearly the same in aqueous and in alcoholic solution; it will be seen below that the same is true of solutions of *d-neo*bornylamine hydrobromide.

### *Benzoyl*-d-*bornylamine.*

This compound is prepared from the hydrobromide by the Schotten-Baumann reaction; it separates from aqueous alcohol in long, glistening needles, melting at 138·5°. Its rotatory-power determinations in ethyl-alcoholic solution yielded the following results:

| | 1·2080 gram in 30 c.c. | | | 0·3016 gram in 30 c.c. | | |
|---|---|---|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
| α ......... | −4·23° | −3·66° | −3·48° | −1·03° | −0·89° | −0·83° |
| [α] ...... | −26·3 | −22·7 | −21·6 | −25·6 | −22·1 | −20·6 |
| [M] ...... | −67·5 | −58·4 | −55·5 | −65·8 | −56·9 | −53·0 |

Rotatory dispersions: 1·216; 1·052. 1·241; 1·072.

Forster (*loc. cit.*) gives the melting point of this substance as 139° and the specific rotation as $[\alpha]_D$ −21·8° in alcoholic solution;

it is thus evident that his preparation was identical with ours. Similar values for the rotatory power were obtained by Frankland and Barrow (T., 1909, **95**, 2035).

It is therefore apparent that condensation with *d*-oxymethylenecamphor provides an easy method for separating pure *d*-bornylamine.

### *Separation of* d-neo*Bornylamine and its Derivatives.*

Reference has been made above to the presence of an extremely soluble material in the mother liquors, from which the *d*-bornylamino-*d*-methylenecamphor had been separated; this material represents the crude *d-neo*bornylamino-*d*-methylenecamphor. In order to separate the latter substance in quantity use was made of a sample of the mixed hydrochlorides of the two amines which had the molecular rotatory power [M] −38·7° for the mercury-green line in dilute aqueous solution, and hence contained about 61 per cent. of *d-neo*bornylamine hydrochloride. This mixture of hydrochlorides was caused to condense with *d*-oxymethylenecamphor in the manner already described, and the condensation product fractionally crystallised first from light petroleum and then from acetone; a quantity of crystalline product, consisting of the small, glistening needles characteristic of *d*-bornylamino-*d*-methylenecamphor, was thus obtained. These fractions are almost insoluble in acetone, and readily yielded the pure *d*-bornylamine derivative when crystallised from alcohol or aqueous alcohol.

After separating as large a quantity as is possible of the *d*-bornylamino-*d*-methylenecamphor from the light petroleum solution, the very soluble material remaining in the mother liquors is recovered by evaporation, and fractionally crystallised from dilute alcohol. In this operation it is important to adjust the concentration of the solution and the proportion of water and alcohol present, so that crystallisation occurs slowly at a temperature just above the ordinary one; a series of lævorotatory fractions is then obtained. In one particular operation five consecutive fractions separated, which had the specific rotatory powers [α] −81·0°, −6·5°, −102·6°, 90·7°, and −76·9° for the mercury-green line in 0·5 per cent. alcoholic solutions at 20°; the third of these proved to be nearly pure *d-neo*bornylamino-*d*-oxymethylenecamphor, and the second contained nearly all of the *d*-bornylamine derivative which had resisted separation during the acetone crystallisation. The four fractions which gave the specific rotatory powers [α] −81·0°, −102·6°, −90·7°, and −76·9° are more nearly identical than is indicated by these values, because the latter are disturbed by the mutarotation. On conversion into the hydrobromide of the base by bromine and alcohol, as previously described, the salts obtained gave the specific rotations $[\alpha]$ $-36·1°$, $-37·0°$, $-36·5°$, and $-34·3°$ respectively in dilute aqueous solution for the mercury-green line.

### d-neo*Bornylamino*-d-*methylenecamphor.*

This compound is obtained in a state of comparative purity by crystallising the highly lævorotatory fractions of the *d*-oxymethylenecamphor condensation product from aqueous alcohol until the rotatory power remains unchanged; it forms characteristic, striated scales, melting at 212°, and retaining a pale yellow colour which cannot be removed by recrystallisation. It is extremely soluble in alcohol, acetone, or light petroleum, and can only be conveniently crystallised from dilute alcohol:

0·1110 gave 0·3234 $CO_2$ and 0·1020 $H_2O$. C = 79·46; H = 10·28.

$C_{21}H_{33}ON$ requires C = 79·93; H = 10·55 per cent.

The rotation constants were determined in ethyl-alcoholic solution containing 0·1009 gram in 30 c.c., with the following results:

| | After 1 hour. | | | After 48 hours. | | |
|---|---|---|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
| $\alpha$ ......... | −1·38° | −1·17° | −1·11° | −1·30° | −1·10° | −1·05° |
| $[\alpha]$ ...... | −103 | −87·0 | −82·5 | −96·6 | −81·8 | −78·0 |
| [M] ...... | −323 | −274 | −260 | −304 | −258 | −246 |
| Rotatory dispersions: | 1·243; 1·054. | | | 1·238; 1·048. | | |

Both this compound and its isomeride strongly resist the action of the ordinary hydrolysing agents.

### d-neo*Bornylamine Hydrobromide.*

This salt is prepared from the foregoing substance by treatment with bromine and alcohol in the usual manner; it separates in hard, glistening, colourless crystals when its acetone solution is concentrated on the water-bath, and may be precipitated from alcoholic solutions in minute crystals by the addition of ether. It is very soluble in water, alcohol, or chloroform, and only moderately so in acetone; it is scarcely more soluble in the latter solvent when hot than in the cold:

0·2622 required 11·1 c.c. $N/10$-$AgNO_3$. Br = 33·83.

$C_{10}H_{19}N,HBr$ requires Br = 34·14 per cent.

The following determinations of rotatory powers were made:

*Solvent: Water.*

| | 0·7410 gram. | | | 0·3004 gram. | | |
|---|---|---|---|---|---|---|
| | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. |
| $\alpha$ ……… | −3·66° | −3·21° | −3·10° | −1·48° | −1·31° | −1·25° |
| $[\alpha]$ …… | −37·0 | −32·5 | −31·4 | −37·0 | −32·7 | −31·2 |
| [M] …… | −86·6 | −76·1 | —73·5 | −86·6 | −76·5 | −73·0 |

Rotatory dispersions: 1·181; 1·035. 1·184; 1·048.

*Solvent: Ethyl Alcohol.* *Solvent: Chloroform.*

| | 0·4910 gram. | | | 0·2012 gram. | | |
|---|---|---|---|---|---|---|
| $\alpha$ ……… | −2·58° | −2·26° | −2·16° | −1·19° | −1·07° | −1·00° |
| $[\alpha]$ …… | −39·4 | −34·5 | −33·0 | −44·4 | −39·9 | −37·3 |
| [M] …… | −92·1 | −80·7 | −77·2 | −104 | −93·4 | −87 3 |

Rotatory dispersions: 1·194; 1·046. 1·190; 1·070.

### d-neo*Bornylamine.*

The aqueous solution of the above hydrobromide is treated with sodium hydroxide and extracted with light petroleum; after evaporating off the solvent and leaving for some time in a vacuum, any remaining traces of petroleum are removed by heating for a few minutes at 100°. The substance thus obtained exhibited the properties stated by Forster, and melted at 181°; the rotation constants were determined in alcoholic solution, 1·3239 grams being contained in 30 c.c.

| | $\text{Hg}_{\text{green}}$. | $\text{Hg}_{\text{yellow}}$. | $\text{Na}_{\text{yellow}}$. |
|---|---|---|---|
| $\alpha$……… | −7·84° | −6·97° | −6·70° |
| $[\alpha]$…… | −44·4 | −39·5 | −38·0 |
| [M] … | −67·9 | −60·4 | −58·1 |

Rotatory dispersions: 1·170; 1·040.

The purest sample of *d-neo*bornylamine obtained by Forster gave the value $[\alpha]_D$ −43·7° in a 4 per cent. alcoholic solution; the base which we obtained gave $[\alpha]_D$ −38·0° under the same conditions. Forster's determination was probably made with pure *d-neo*bornylamine, and, if so, our product contained about 94 per cent. of this substance; thus, in spite of the extreme solubility of *d-neo*bornylamino-*d*-methylenecamphor, an approximate separation of the isomeric bases can be achieved by the method now given. With the comparatively small amount of material in our possession it was not practicable to attempt further purification, but it is clear that considerable difficulty would attend the isolation of pure *d-neo*bornylamine by our method alone. It is, however, important to notice that the approximate separation we have effected does not depend on the composition of the initial mixture of the two bases (compare Forster, T., 1900, **77**, 1158), and it may thus be anticipated that a convenient mode of isolating pure *d-neo*bornylamine would result from combining the two methods, using our method for the preliminary separation, and that of Forster for the final purification. It also appears that the approximately pure *d-neo*bornylamine hydrobromide can be further purified simply by repeated crystallisation from acetone.

The values for the rotation constants of the *d-neo*bornylamine derivatives given do not, of course, refer to pure materials, but they may be advantageously quoted in view of the paucity of data available for this interesting base. The benzoyl derivative prepared from our specimen melted at 112—115°, and gave the values $[\alpha] -60{\cdot}2°$, $-52{\cdot}1°$, and $-50{\cdot}0°$ for the mercury-green, mercury-yellow, and sodium-yellow rays respectively in a 1·8 per cent. alcoholic solution; Forster gives $[\alpha]_D -44{\cdot}7°$ under these conditions.

### *Condensation of* l-*Oxymethylenecamphor with the Bornylamines.*

It was hoped that on condensing the mixture of *d*-bornylamine and *d-neo*bornylamine with *l*-oxymethylenecamphor, the order of solubility of the two products might be the reverse of that observed when *d*-oxymethylenecamphor is used. *d-neo*Bornylamino-*l*-methylenecamphor proved, however, to be more soluble than *d*-bornylamino-*l*-methylenecamphor, and both were found to be more soluble than the isomerides containing the *d*-methylenecamphor residue; a long series of fractional crystallisations showed that no advantage was to be gained by the application of *l*-oxymethylenecamphor to the separation.

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## LIII.—*The Mode of Combustion of Carbon.*

By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

IN previous papers ("The Rate of Reduction of Carbon Dioxide by Carbon," T., 1912, **101**, 831; "The Combustion of Carbon," T., 1912, **101**, 846) we have shown that a consideration of the relative rates of the various reactions between oxygen, carbon monoxide, carbon dioxide, and carbon leads to the conclusion that, in the burning of carbon, the two oxides are produced simultaneously. That is to say, neither is the "primary" product of oxidation of carbon in the sense that it takes precedence over the other. It was left to a succeeding paper to explain the manner in which this simultaneous production of the two oxides takes place.

In the present paper we describe experiments designed to solve this problem, and, on the strength of these experiments, we put forward an hypothesis as to the manner in which solid carbon burns, which appears to us to leave no known fact unexplained.

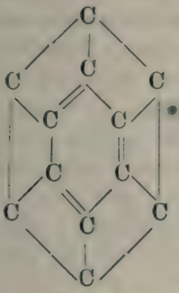
The experiments show that carbon, at all temperatures up to 900° and probably above that temperature, has the power of pertinaceously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner it appears, not as oxygen, but as carbon dioxide and carbon monoxide. The proportions in which it appears in these two oxides when completely removed depend on the temperature at which the carbon has been heated during oxygen-fixation.

No physical explanation alone can account for this "fixation" of oxygen, but, in all probability, it is the outcome of a physico-chemical attraction between oxygen and carbon. Physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which, indeed, shows progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means.

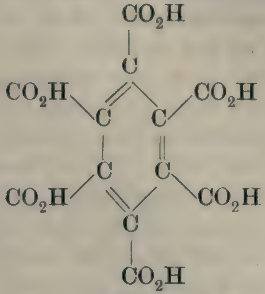
Decomposition of the complex by heat produces carbon dioxide and carbon monoxide. At a given temperature of decomposition these oxides make their appearance in a given ratio. Further, when a rapid stream of air at a given temperature is passed over carbon (which has previously been "saturated" with oxygen at that temperature), carbon dioxide and carbon monoxide appear in the products of combustion in nearly the same ratio as they do in the products of decomposition of the complex at that temperature.

Our hypothesis is that the first product of combustion of carbon is a loosely formed physico-chemical complex, which can be regarded as an unstable compound of carbon and oxygen of an at present unkonwn formula, $C_xO_y$. It is probable that no definite formula can be assigned to this complex.

Our conception of what takes place during the combustion of carbon is, briefly, as follows: each oxygen molecule that comes into collision with the carbon becomes "fixed," in so far as it is rendered incapable of further progress by the attraction of several carbon molecules. We have as yet no absolute knowledge of the number of atoms contained in the carbon molecule. The formation of benzenehexacarboxylic acid (mellitic acid) by the oxidation of either amorphous carbon or graphite, warrants the assumption that the carbon molecule contains not less than twelve atoms, possibly arranged in the following manner (Dewar, *Chem. News*, 1908, **97**, 16):

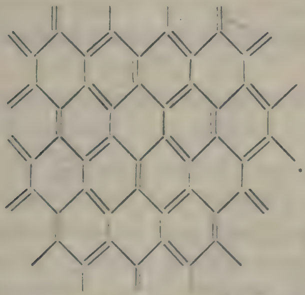


Carbon.



Mellitic acid.

According to Aschan (*Chem. Zeit.*, 1909, **33**, 561), this representation of the molecule of carbon as two concentric benzene nuclei does not harmonise with the strain theory; for whilst carbon is an exceedingly stable substance, the strain in such a molecule must be greater even than that in a molecule of an explosive substance such as acetylene. On several grounds, which are discussed at length in the original paper, Aschan suggests an unstrained arrangement of benzene nuclei of the following type:



It may be, therefore, that in the oxidation of carbon the oxygen molecule actually *enters* the carbon molecule, a rearrangement of atoms taking place. However, for the present it is sufficient to assume that several carbon molecules hold one oxygen molecule, in bond as it were, and do not allow it to escape in conjunction with one of their atoms. A considerable evolution of heat takes place during this attachment of oxygen molecules, so much so that some of them eventually acquire sufficient energy to seize hold of a carbon atom and depart with it as carbon dioxide. Some of them become torn apart in the process—become atomised—and leave the carbon molecule as carbon monoxide.

This formation of a complex, and partial decomposition as fresh oxygen molecules become attached, goes on until the carbon becomes "saturated," the products of combustion during this period (a comparatively short one) being $C_xO_y$, $CO_2$, and CO. After the carbon has become saturated there is an alternate formation and decomposition of the complex. Each oxygen molecule that impinges on the carbon is at once seized hold of to form the complex, but the energy set free when this occurs decomposes an equivalent proportion of the complex formed from previous oxygen molecules. So that, finally, when air is passed over saturated carbon maintained at a constant temperature by the application of an external source of heat, carbon dioxide and carbon monoxide appear in the products of combustion in volume sufficient to account for the total volume of oxygen in the air originally passed.

In the normal burning of carbon, therefore, the carbon dioxide and carbon monoxide found as the apparently primary products of combustion, arise from the decomposition, at the temperature of combustion, of a complex the formation of which is the first result of the encounters between oxygen and carbon molecules.

The idea of "oxygenation" of the combustible as a preliminary to definite chemical reaction is not without precedent.

The researches of W. A. Bone and his co-workers on the combustion of hydrocarbons point unmistakably to a preliminary *entrance* of the oxygen into the molecule of the combustible, an unstable complex being formed, which breaks up immediately into definite chemical compounds.

Thus, in the case of methane the scheme of reaction is probably:

$$CH_4 + O_2 = (CH_4O_2) = H\cdot CHO + H_2O.$$

Formaldehyde has been isolated during the slow combustion of methane over a heated surface and in the flame of methane burning in air, and its presence has been indicated during the propagation of "inflammation" in explosive mixtures of methane and oxygen. Moreover, there is no evidence of any essential difference between the "detonation" and "inflammation" of the paraffins, so far as the result of the *initial* encounters between molecules of hydrocarbon and oxygen is concerned. That is to say, even for the most rapid oxidation, the transitory formation of oxygenated complexes may take place.

There seems to us to be nothing to conflict with the supposition that in general it will be found that the initial encounters between oxygen and a combustible material result in the "fixation" of the oxygen, and that the products of combustion that make their appearance are the result of decomposition of a complex first formed. It may be pointed out that the work of Dixon, referred to in a previous paper, on the explosion of the gaseous carbon compounds as exemplified by cyanogen, shows merely that in this case carbon monoxide is produced before carbon dioxide; it does not in any way negative the possibility of the transitory formation of an intermediate combination.

## EXPERIMENTAL.

Reference to our previous paper on the combustion of carbon (*loc. cit.*, p. 850) will recall the fact that in determining the rate of oxidation of carbon at different temperatures, great care had to be taken that the carbon surface was in a "normal" condition of activity, such as was obtained after air or oxygen had been circulated over it during a long time at the experimental temperature. In this way alone could the relativity of the results be trusted; for it was noted that when the carbon surface had been subjected to prolonged exhaustion at a high temperature before being brought to the experimental temperature, the rate of disappearance of oxygen at that temperature was abnormally rapid.

As an instance of this we may give the details of an experiment with air at 350°, made after the carbon had been exhausted at a temperature of 950° during several hours.

The rate of disappearance of oxygen is given by the equation: $1/t\,.\,\log C_0/C_t=k$.

*Air over Carbon at* 350°. *Carbon surface previously exhausted at* 950°.

| Time. | $P_{O_2}$. | $k$ ($t=1$ minute). |
|---|---|---|
| 0 | 89·0 | — |
| 15 | 80·5 | 0·00291 |
| 30 | 77·4 | 0·00202 |
| 90 | 71·3 | 0·00107 |
| 150 | 67·7 | 0·00079 |
| 210 | 64·0 | 0·00068 |
| 270 | 61·0 | 0·00061 |
| 290 | 56·3 | 0·00051 |

It will be seen that the value of $k$ decreases rapidly throughout the experiment, showing a much greater disappearance of oxygen during the first fifteen minutes than over any subsequent period. The "normal" value of $k$ at 350°, which is ultimately attained after several charges of air have been circulated over the carbon surface, is 0·0000546.

It appeared that the rapid fall in pressure in the apparatus during the first few minutes after the air was admitted to the "exhausted" carbon took place before any products of combustion of the carbon could have been carried by the circulating current to the absorption tube for the removal of carbon dioxide. We therefore made a number of experiments in which no attempt was made to remove any carbon dioxide formed, but in which the course of the reaction was followed by the analysis of samples of the gases shut off from the circuit at definite intervals of time (see diagram, *loc. cit.*, p. 835). A typical example of such an experiment is given below.

*Air over Carbon at* 400°. *Carbon surface previously exhausted at* 950°. *Carbon dioxide not removed.*

| | P. | Gas analysis. | | | $P_{CO_2}$. | $P_{O_2}$. | $P_{CO}$. |
|---|---|---|---|---|---|---|---|
| Time. | mm. | $CO_2$. | $O_2$. | CO. | mm. | mm. | mm. |
| 0 | 477·4 | nil. | 20·70 | nil. | — | 98·9 | — |
| 5 | 469·0 | 9·10 | 0·30 | 4·65 | — | — | — |
| 60 | 465·5 | 6·10 | 9·90 | 2·55 | 28·3 | 46·0 | 11·8 |
| 240 | 463·0 | 9·65 | 4·90 | 3·50 | 44·7 | 22·8 | 16·9 |
| 360 | 461·0 | 11·00 | 3·15 | 3·65 | 49·6 | 15·5 | 18·4 |

No partial pressures can be calculated from the analysis of the sample taken after five minutes, for it does not, of course, represent the average of the contents of the apparatus. It can be regarded as representing the average composition of the first two or three hundred c.c. of air drawn through the heated carbon. It will be seen that it contained only 0·30 per cent. of oxygen, and that the amount of carbon dioxide and carbon monoxide formed in no way makes up the balance of the oxygen that has disappeared. Moreover, there is a *reduction* of pressure of 8·4 mm., whereas, since the carbon dioxide was not being removed and a certain quantity of carbon monoxide was formed, there should have been an increase.

The samples taken at the end of 60, 240, and 360 minutes more nearly represent the average contents of the apparatus, and the partial pressures of carbon dioxide, oxygen and carbon monoxide calculated from them should be approximately correct. Now, since no product of combustion has been removed, the oxygen-content of the gases in the apparatus, as represented by a sample of the products of combustion at any stage in the experiment, should be the same as that of the air originally introduced. Calculation gives the following results:

| | Oxygen content. mm. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Time. | $CO_2$. | | $O_2$. | | CO. | | | Disappearance of oxygen mm. |
| (Original air) 0 | nil | + | 98·9 | + | nil | = | 98·9 | — |
| 60 | 28·3 | + | 46·0 | + | ½(11·8) | = | 80·2 | 18·7 |
| 240 | 44·7 | + | 22·6 | + | ½(16·9) | = | 75·9 | 23·0 |
| 360 | 49·6 | + | 15·5 | + | ½(18·4) | = | 74·2 | 24·6 |

As a check on these results calculation can be made of the total reduction in pressure observed in the apparatus at the time the samples were taken; thus, at the end of sixty minutes there was a contraction of 11·9 mm.; but 11·8 mm. of carbon monoxide have been formed, which should have shown an expansion of 5·9 mm. The total contraction observed, therefore, is 17·8 mm., which compares quite well with the amount of disappearance of oxygen calculated from the gas analysis. Similarly, at times 240 and 360 the total contraction observed was 22·8 and 25·6 mm. respectively.

At the end of three hundred and sixty minutes the circulation was stopped and the reaction-tube exhausted, the temperature being maintained at 400°. The temperature was then rapidly raised to 950°, exhaustion being continuous. Ninety-five and a-half c.c. of gas were evolved from the carbon and collected at the pump. This gas contained:

| | |
|---|---|
| Carbon dioxide | 7·35 per cent. |
| Oxygen | nil. |
| Carbon monoxide | 91·70. |
| Nitrogen | 0·95 (by difference). |

The oxygen-content of this mixture is 53·2 c.c. Since the capacity of the circulation apparatus was 1580 c.c., this corresponds with a pressure of 25·5 mm., which is the total amount of contraction observed during the experiment.

It hardly seemed possible that the exhausted charcoal was capable, when at a temperature of 400°, of occluding or condensing gases in its pores in the same manner as it does at 0°. However, to test this point we made experiments in which the carbon, previously exhausted at 950°, was brought to a temperature of 400°, and treated in the circulation apparatus with (1) carbon dioxide, and (2) carbon monoxide at that temperature. After treatment with each of these gases (during which no absorption of either could be detected), the apparatus was exhausted, the temperature of the carbon being maintained at 400°, and an experiment made with air in the same manner as that recorded above. The result was, in every case, similar to those obtained when the "exhausted" carbon had not been previously treated with carbon dioxide or carbon monoxide at 400°.*

It would appear, therefore, that when oxygen or air is brought into contact at a temperature of 400° with pure carbon which has been freed from all gases by exhaustion at a high temperature, the first thing that happens is a fixation of the oxygen; and that this oxygen cannot be removed as such by exhaustion at 400°, but appears as oxides of carbon when the temperature of the latter is raised.

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* For example, in an experiment made after treatment of the surface with carbon dioxide, there was a disappearance of oxygen amounting to 22·6 mm. after 360 minutes' circulation. On raising the temperature to 950°, 88·9 c.c. of gas were evolved containing per cent., $CO_2$ 6·85; $O_2$ nil; CO 92·05; $N_2$ 1·10. The oxygen-content of this gas is 47·1 c.c., which is equivalent to a pressure in the circulation apparatus of 22·9 mm.—the amount of contraction observed during the experiment.

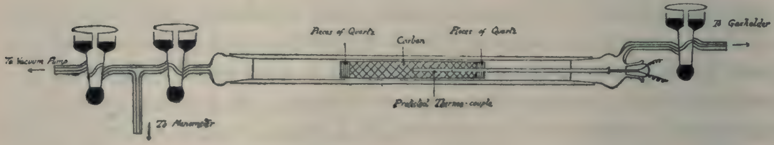
It may be remarked that this fixation of oxygen is effected, not only by charcoal, but also by graphite, although to a less extent.

### *The Fixation of Oxygen by Carbon.*

It appeared that further information regarding what takes place when oxygen is first admitted to heated carbon might be forthcoming from an extended examination of the products of combustion at different temperatures. For this purpose the "circulation" method of experiment was not altogether suitable, for, as a preliminary, we required to obtain some definite idea of the rate of disappearance of oxygen during the first few minutes after its admission to the heated carbon.

The apparatus used for this preliminary series of experiments is shown in Fig. 1. The carbon was packed in a quartz tube 14 cm. long and of 1·6 cm. internal diameter, which just fitted into a porcelain tube 52 cm. long. This porcelain tube had a ground joint at either end, making connexion on the one hand with a gas-holder, and on the other with an automatic Sprengel mercury pump and a mercury manometer. The latter consisted simply of a fairly wide tube of barometric height standing in a trough of mercury.

FIG. 1.



The porcelain tube was heated in an electric resistance tube-furnace, the temperature of which was maintained constant by means of Nernst lamp resistances in the manner described in previous papers. A platinum and platinum-rhodium thermo-couple passed through a glass plug fitted to one of the end connexions of the porcelain tube (see diagram), the junction being contained in a thin sheath of quartz embedded in the carbon. The temperatures were determined from the deflections of a sensitive "Broca" mirror galvanometer on a scale 40 cm. in length.

The method of experiment was as follows. The apparatus having been thoroughly exhausted with the reaction tube at a temperature of 1000°, the latter was brought to the experimental temperature and the tap leading to the vacuum pump closed. The tap leading to the gas-holder, in which pure oxygen was stored over concentrated sulphuric acid, was then opened during exactly five seconds. At the end of fifteen seconds the first reading of the manometer was taken,* and from then onwards simultaneous readings were taken of the temperature of the carbon and the pressure in the apparatus at frequent intervals. The initial pressure which should prevail in the apparatus as soon as the oxygen was admitted was calculated from the known volume of the apparatus and the volume of the oxygen used, a preliminary series of experiments with known volumes of nitrogen having been made with the apparatus heated at different temperatures to determine the amount of expansion.

The results can be expressed in tabular form as follows:

| Experimental temperature... | 300°. | | | 350°. | | | 400°. | | | 500°. | | | 600°. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time: minutes. | Pressure, mm. | Temperature. | Percentage contraction. | Pressure, mm. | Temperature. | Percentage contraction. | Pressure, mm. | Temperature. | Percentage contraction. | Pressure, mm. | Temperature. | Percentage contraction. | Pressure, mm. | Temperature. | Percentage contraction. |
| 0·00 | 734 | 300° | — | 754 | 350° | — | 879 | 400° | — | 762 | 500° | — | 713 | 600° | — |
| 0·25 | 587 | — | — | 622 | — | — | 744 | — | — | 682 | — | — | 687 | — | — |
| 0·50 | 573 | 380 | 21·9 | 611 | 425 | 19·0 | 728 | 460 | 17·2 | 668 | 540 | 12·3 | 671 | 620 | 5·9 |
| 0·75 | 565 | — | — | 604 | — | — | 721 | — | — | 659 | — | — | 667 | — | — |
| 1·00 | 560 | — | 23·6 | 598 | 410 | 20·7 | 715 | 445 | 18·6 | 656 | 535 | 13·9 | 665 | 620 | 6·7 |
| 1·25 | 556 | 360 | 24·2 | 594 | — | 21·2 | 712 | 415 | 19·0 | 654 | — | 14·1 | 663 | 610 | 7·0 |
| 2 25 | 546 | 350 | 25·6 | 583 | 400 | 22·7 | — | — | — | 647 | — | 15·0 | 659 | 610 | 7·6 |
| 5·25 | 531 | 340 | 27·6 | 567 | 380 | 24·8 | 685 | 405 | 22·1 | 637 | 530 | 16·4 | 653 | 605 | 8·5 |
| 15·25 | 508 | — | 30·6 | 539 | 375 | 28·5 | 658 | 402 | 25·1 | — | — | — | 642 | 605 | 10·0 |
| 30·25 | 481 | 320 | — | 510 | 360 | — | 626 | 400 | — | — | — | — | 634 | 605 | — |
| 60·25 | 452 | 300 | — | 474 | 350 | — | 596 | 400 | — | — | — | — | 625 | 600 | — |
| 120·25 | 429 | 300 | 41·4 | 445 | 350 | 41·0 | 565 | 400 | 35·7 | 590 | 500 | 22·6 | 615 | 600 | 13·8 |

The rate of disappearance of oxygen during the first fifteen seconds is extremely rapid, after which a slow absorption takes place, continuing over several hours.

This is well shown in the curves in Fig. 2. It will be seen that at each temperature the type of curve is the same—the rapid fall in pressure during the first fifteen seconds bearing the same proportion in each case to the total fall at the end of fifteen minutes. The difference between the results at different temperatures would therefore appear to lie, not in the *rate* of fixation of oxygen, but in the *amount* fixed. That is to say, the proportion of the oxygen present that can become fixed at different temperatures becomes so, *ceteris paribus*, in about the same length of time.

This rather points to a physical explanation of what is taking place; a physical absorption or adsorption of the oxygen, followed, possibly, by chemical change within the carbon. If this were so, however, one would expect that a reduction in pressure alone should suffice to remove either the "absorbed" oxygen or the products of its chemical reaction after absorption; and, if those products are carbon dioxide and carbon monoxide, there seems no reason why the admission of either of these two gases to "exhausted" carbon should not result in some absorption of them, at any rate at the lower temperatures.

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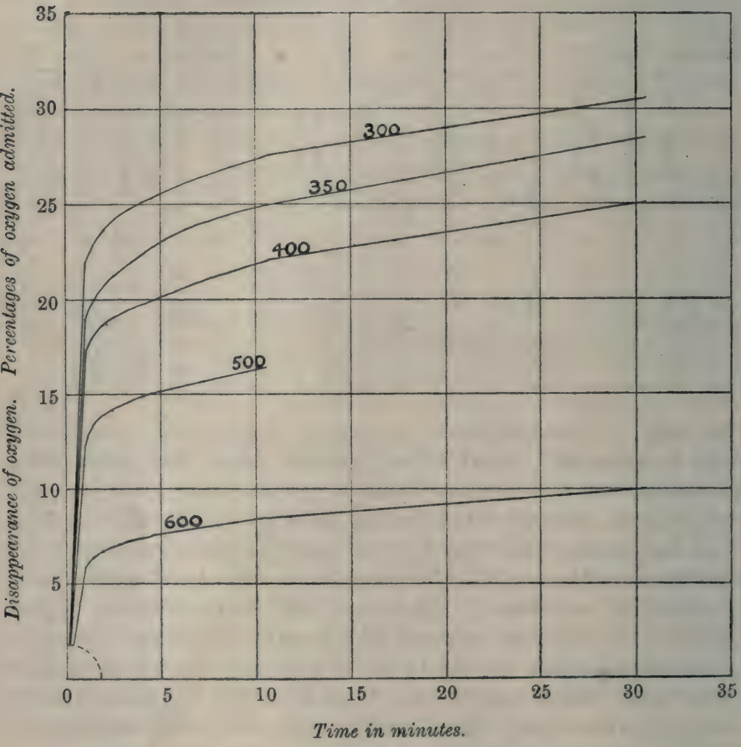
* The oscillations of the mercury in the manometer prevented accurate readings from being made before this time.

Such, however, is not the case; we were unable to observe any reduction in pressure in the apparatus when either carbon dioxide or carbon monoxide was admitted to the carbon at a temperature of 250°; nor, on raising the temperature after the apparatus had been exhausted at 250°, were any traces of gas driven off. Moreover, in experiments in which the carbon was treated with either of these gases at 250°, and the apparatus then exhausted at that temperature, the carbon was found to be in the same reactive state towards oxygen as when it had not been so treated.

FIG. 2.



Another point which may perhaps argue against a physical condensation of oxygen in the pores of the charcoal is the heating effect observed. This, it will be noticed, becomes less pronounced the higher the initial temperature of the carbon. That is to say, the heating effect is less when the proportion of the oxygen admitted that becomes "fixed" is less.

### *Experiments Regarding the Nature of "Fixed" Oxygen.*

The attraction between the oxygen and carbon molecules appeared to be greater than could be explained on the hypothesis that it was a purely physical attraction. We sought, therefore, for some means by which its chemical nature, supposing it partook of such, could be demonstrated.

In the first place it seemed desirable to determine the weight of oxygen that a given weight of carbon would retain at any particular temperature.

A quartz vessel having a narrow inlet-tube for air, that could be closed by a tap of quartz, and a wider exit-tube through which the carbon could be introduced, was loosely filled with 9·7 grams of purified wood charcoal sieved so as to pass through a 60-mesh sieve and remain on a 100-mesh. This bulb was heated in an electric resistance furnace at a temperature of 300°, and dry air slowly drawn through it during six hours. At the end of that time a sample of the gases that passed through was analysed, and since its oxygen-content was found to correspond with that of the air entering, the "fixation" of oxygen was considered to have ceased.

The bulb was then exhausted at a temperature of 300°, the temperature rapidly raised to 1000°, and the gases evolved collected in two portions. The first portion measured (at 0° and 760 mm.) 111·5 c.c., and the second 32·2 c.c. The analyses were:

| Volume. | First portion.<br>111·5 c.c. | Second portion.<br>32·2 c.c. |
|---|---|---|
| Carbon dioxide ......... | 22·60 | 12·15 per cent. |
| Oxygen .................. | nil. | nil. |
| Carbon monoxide ...... | 76·90 | 87·35 ,, ,, |

The oxygen-content of the whole of the gas collected was, therefore, 85·0 c.c. A repetition of the experiment, using the same weight of carbon, gave the volume of oxygen "fixed" as 88·9 c.c.

The weight of oxygen retained by 12 grams of carbon would therefore be (at 300°) 0·16 gram. That is to say, a formula $C_{100}O$ could be assigned to the combination. This, however, only refers to the particular temperature of 300°.

A definite chemical compound, if it is decomposable at all at one temperature, should be wholly decomposed at that temperature if the products of its decomposition are continuously removed. To be quite certain regarding this point, we made a series of experiments in the apparatus just described, in which the carbon was charged with oxygen at 300° by drawing air through it in a slow stream during two hours. Fractional removal of the gases evolved on raising the temperature was then made, with the following results:

| Temperature of removal of gas. | Volume of gas evolved. C.c. | Analysis. $CO_2$. | $O_2$. | CO. | Oxygen-content. C.c. |
|---|---|---|---|---|---|
| 300— 400° | 14·0 | 57·00 | nil. | 42·35 | 10·2 |
| 400— 500 | 16·7 | 41·55 | ,, | 57·95 | 10·8 |
| 500— 600 | 23·4 | 30·25 | ,, | 69·30 | 14·0 |
| 600— 700 | 32·6 | 14·55 | ,, | 85·00 | 17·2 |
| 700— 800 | 21·3 | 3·45 | ,, | 96·05 | 10·0 |
| 800—1000 | 36·7 | 0·75 | ,, | 98·70 | 16·8 |

The duration of heating and removal of the fractions was six hours at temperatures below 700°; above that temperature it was twelve hours, for minute traces of gas continued to appear at the end of six hours.

These figures, at first sight, seem to negative the idea that the oxygen forms a definite chemical compound with the carbon when it becomes "fixed." It is conceivable, however, that at each fractionation temperature the products of decomposition are carbon dioxide, carbon monoxide, and a third substance which remains undecomposed at that temperature, and is less complicated than the original substance. If this were so, however, every small increment in temperature must be regarded as causing the degradation of one compound and the formation of another, for (as other experiments not detailed here have shown) carbon containing "fixed" oxygen, from which no gas can be extracted at a given temperature, evolves a small quantity of gas when its temperature is raised but a few degrees.

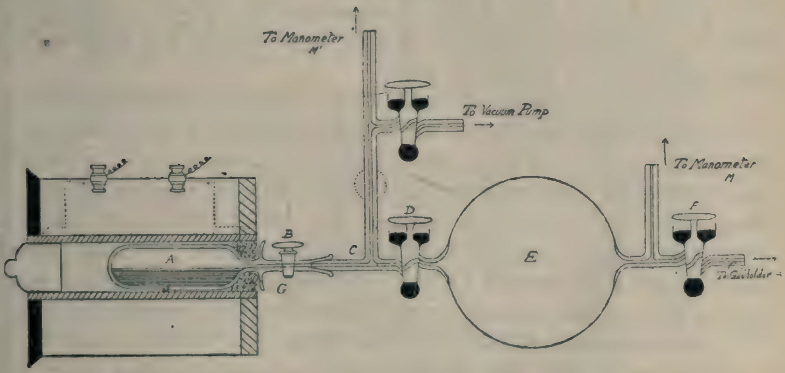
As arguing against a purely physical explanation, on the other hand, it will be noted that the oxygen-content of the gases evolved at different temperature increases up to 700° for every 100° rise in temperature, and then decreases, the greatest evolution taking place between 500° and 700°. This is not what one would expect from a purely physical association of the oxygen with the carbon. In that case, since the quantity of oxygen associated would be a direct function of the temperature, equal increments of temperature should result in regularly decreasing quantities of oxygen evolved.

On the whole, it appears most probable that a loosely-formed complex is formed, to which no definite formula can be assigned, one oxygen molecule (or atom) being held by the attraction, partly chemical and partly physical, of several carbon atoms or molecules. That the oxygen must be partly in the atomic condition seems to follow necessarily from the fact that the decomposition of the complex yields, even at low temperatures, a certain amount of carbon monoxide.

### *The Distribution of Oxygen between the Products of Combustion of Carbon.*

We have already stated that in the experiments just described there was formed, at all temperatures, a certain quantity of the gaseous oxides of carbon as well as the complex during the fixation of oxygen. It seemed to us that considerable information could be obtained from a determination of the proportions in which a known volume of oxygen, when admitted to carbon at different temperatures, appeared in the products of combustion as carbon dioxide, carbon monoxide, and the hypothetical complex, which, for convenience, we will call $C_xO_y$. For this purpose it was essential that accurate measurements should be made of the volume of oxygen originally admitted to the heated carbon, and of the gases remaining at the end of a definite interval of time. Further, it was necessary that the carbon could be rapidly raised in temperature to 1000° to decompose the complex.

FIG. 3.



The apparatus used for these experiments is shown in Fig. 3.

The carbon, weighing just under five and a-half grams, was contained in a stout-walled bulb of quartz (*A*), of about 50 c.c. capacity, and occupied about one-third of its volume. This bulb could be closed by a quartz tap (*B*), and was connected by a ground joint to a ⊤-piece (*C*), one branch of which led to a mercury manometer (*M′*) and vacuum pump, and the other, through a mercury-cup tap (*D*) to a globe (*E*) of 649 c.c. capacity. The globe was closed by another mercury-cup tap (*F*), through which it could be filled with oxygen, and was fitted with a mercury manometer (*M*).

The bulb was heated in an electric resistance furnace the refractory tube of which was wound with fine platinum wire, the coils at the end through which the neck of the bulb passed being placed close together to compensate for loss of heat by radiation from the furnace at that end, which was purposely left unprotected by heat-insulating material. This arrangement enabled a zone of uniform temperature to be obtained throughout that portion of the furnace occupied by the bulb; that is to say, over a distance of 11 cm. starting 4 cm. from the mouth of the furnace.

The quartz tap was kept cold by a rapid stream of water, which was prevented from entering the furnace by a quartz collar ($G$) fused to the neck of the bulb.

Temperatures were measured by means of a platinum and platinum-rhodium thermo-couple passing along the furnace tube, the junction being at $J$, and were maintained constant as before by the use of Nernst steadying-resistances.

*Method of Conducting an Experiment.*—The whole apparatus having been thoroughly exhausted, with the carbon heated to 1000°, tap $D$ and the tap leading to the vacuum pump were closed. The globe $E$ was then filled at atmospheric pressure with oxygen from a gas-holder, in which it had been stored for several days over concentrated sulphuric acid.

The carbon was then brought to the experimental temperature, and oxygen admitted to it by rapidly opening tap $D$ leading to the globe, and leaving it open during five seconds. The oxygen was heated in contact with the carbon during a given length of time, readings of the manometer $M'$ being taken at definite intervals. Tap $B$, leading to the reaction-chamber, was then closed, and the gases contained in the manometer and connexions withdrawn, measured, and analysed separately as "manometer gas." This gas contained, besides unburnt oxygen, a certain quantity of carbon dioxide and carbon monoxide that had diffused from the reaction-chamber.

The gases in the reaction-chamber were then pumped out, exhaustion being continued with the carbon maintained at the experimental temperature during half-an-hour, at the end of which time no further traces of gas appeared.* The volume of these gases was measured and an analysis made ("final gas").

As soon as the "final gas" had been withdrawn, the temperature of the carbon was raised to 1000—1050°, and maintained at that temperature during one hour, exhaustion and collection of the gases evolved being continued throughout. Great care was taken in the comparative experiments that the rate at which the tempera-

---

* In experiments at temperatures above 800° minute bubbles of gas continued to be removed by the pump at the end of half an-hour, and exhaustion was continued in these cases during one hour.

### SERIES I.—*Pure Oxygen.*

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature °C. ......... ..... .. | 100 | 200 | 300 | 350 | 400 | 450 | 500 | 550 | 600 | 650 | 700 | 750 | 800 | 900 | |
| Volume of oxygen burned, c.c. | 18·67 | 32·30 | 35·84 | 34·21 | 27·07 | 31·47 | 20·64 | 17·50 | 15·18 | 19·65 | 16·29 | 17·38 | 13·75 | 11·37 | |
| "*Manometer Gas.*" | | | | | | | | | | | | | | | |
| Volume c.c. .................. | 10·14 | 8·90 | 8·35 | 10·79 | 11·50 | 13·76 | 14·78 | 16·66 | 17·29 | 14·41 | 14·06 | 17·25 | 16·31 | 16·52 | |
| Analysis, $CO_2$, per cent. ... | 3·55 | 4·00 | 7·45 | 7·05 | 6·35 | 5·30 | 7·15 | 5·10 | 6·80 | 5·40 | 4·95 | 6·00 | 7·60 | 10·15 | |
| $O_2$ ,, ... | 91·87 | 89·65 | 85·90 | 86·95 | 89·35 | 89·85 | 87·40 | 90·35 | 87·20 | 87·90 | 91·30 | 89·30 | 86·60 | 77·45 | |
| CO ,, | 0·07 | 1·40 | 1·90 | 1·95 | 0·80 | 1·15 | 2·20 | 1·35 | 2·70 | 0·60 | 0·50 | 0·35 | 1·15 | 8·00 | |
| "*Final Gas.*" | | | | | | | | | | | | | | (*a*)* | (*b*) |
| Volume c.c. .................. | 33·80 | 21·95 | 17·63 | 17·57 | 14·55 | 17·46 | 11·14 | 11·07 | 9·34 | 13·76 | 12·06 | 14·32 | 13·61 | 13·22 | 0·95 |
| Analysis, $CO_2$, per cent.... | 9·55 | 41·95 | 75·00 | 73·30 | 73·80 | 69·50 | 66·05 | 55·40 | 68·45 | 81·55 | 83·55 | 74·20 | 50·15 | 8·50 | 1·50 |
| $O_2$ ,, ... | 84·10 | 42·80 | 0·20 | nil | nil | nil | nil | nil | nil | nil | nil | nil | nil | nil | nil |
| CO ,, ... | 0·20 | 6·85 | 16·50 | 19·75 | 20·25 | 24·50 | 29·20 | 29·55 | 27·35 | 12·95 | 11·65 | 20·95 | 45·00 | 87·85 | 98·00 |
| "$C_xO_y$ *Gas.*" | | | | | | | | | | | | | | | |
| Volume, c.c. .............. | 25·00 | 36·35 | 35·58 | 33·29 | 25·42 | 29·96 | 20·08 | 14·23 | 11·81 | 12·91 | 9·37 | 8·11 | 5·00 | 3·30 | |
| Analysis, $CO_2$, per cent.... | 22·00 | 21·15 | 16·15 | 13·20 | 11·50 | 10·00 | 8·75 | 8·35 | 5·75 | 4·55 | 4·45 | 3·70 | 2·00 | 0·65 | |
| CO ,, | 76·40 | 78·40 | 82·85 | 86·30 | 87·90 | 89·50 | 86·70 | 91·25 | 92·15 | 95·00 | 94·05 | 96·00 | 97·50 | 98·85 | |
| Percentage of oxygen burned appearing as : | | | | | | | | | | | | | | | |
| (1) $CO_2$ .................... | 19·25 | 29·60 | 38·6 | 39·8 | 42·3 | 40·9 | 40·7 | 46·2 | 49·8 | 61·0 | 65·9 | 67·1 | 58·8 | 24·6 | |
| (2) CO .. .................... | 0·15 | 2·50 | 4·3 | 5·4 | 5·7 | 7·0 | 8·7 | 10·0 | 9·9 | 4·8 | 4·5 | 8·8 | 22·8 | 60·9 | |
| (3) $C_xO_y$ .................... | 80·60 | 67·90 | 57·1 | 54·8 | 52·0 | 52·1 | 50·6 | 43·8 | 40·3 | 34·2 | 29·6 | 24·1 | 18·4 | 14·5 | |

* The last traces of the "Final Gas" at 900°, collected during one hour's exhaustion, were measured and analysed separately, as shown.

### SERIES II.—*Oxygen*, 50 *per cent.*; *Nitrogen*, 50 *per cent.*

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature °C. | 300 | 350 | 400 | 450 | 500 | 550 | 600 | 650 | 700 | 800 |
| Volume of oxygen burned, c.c. | 14·79 | 14·76 | 13·83 | 12·88 | 12·41 | 11·40 | 10·86 | 10·35 | 9·74 | 8·76 |
| "*Final Gas.*" | | | | | | | | | | |
| Volume, c.c. | 19·42 | 19·44 | 19·70 | 18·53 | 19·17 | 18·30 | 17·75 | 16·68 | 16·12 | 16·71 |
| Analysis, $CO_2$, per cent. | 19·35 | 20·50 | 20·85 | 22·30 | 22·95 | 23·55 | 24·35 | 29·75 | 31·10 | 26·55 |
| $O_2$ ,, | nil | 0·10 | 0·10 | nil | nil | nil | nil | nil | nil | nil |
| CO ,, | 3·60 | 5·20 | 6·35 | 7·75 | 9·90 | 12·95 | 14·35 | 11·00 | 11·05 | 20·95 |
| "$C_xO_y$ *Gas.*" | | | | | | | | | | |
| Volume, c.c. | 18·49 | 18·11 | 16·20 | 14·42 | 12·83 | 11·08 | 9·98 | 8·12 | 7·40 | 5·05 |
| Analysis, $CO_2$, per cent. | 15·65 | 13·95 | 12·75 | 11·75 | 10·35 | 7·25 | 6·40 | 4·75 | 4·10 | 2·60 |
| CO ,, | 84·30 | 85·65 | 86·95 | 88·05 | 89·50 | 92·30 | 92·95 | 94·15 | 95·80 | 97·20 |
| Percentage of oxygen burned appearing as: (1) $CO_2$ | 25·4 | 27·0 | 29·7 | 32·1 | 35·5 | 37·8 | 39·8 | 48·0 | 51·5 | 50·6 |
| (2) CO | 2·4 | 3·4 | 4·5 | 5·5 | 7·5 | 10·4 | 11·7 | 8·7 | 9·1 | 20·0 |
| (3) $C_xO_y$ | 72·2 | 69·6 | 65·8 | 62·4 | 57·0 | 51·8 | 48·5 | 43·3 | 39·4 | 29·4 |

The duration of heating in each experiment was half an hour.

### SERIES III.—*Air.*

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature °C. | 200 | 300 | 400 | 450 | 500 | 550 | 600 | 650 | 700 | 800 | 900 |
| Volume of oxygen burned, c.c. | 7·06 | 6·21 | 5·60 | 5·04 | 4·90 | 4·00 | 4·28 | 3·86 | 3·55 | 3·23 | 2·88 |
| "*Final Gas.*" | | | | | | | | | | | |
| Volume, c.c. | 27·85 | 24·62 | 23·05 | 20·46 | 20·46 | 17·56 | 18·90 | 17·42 | 16·74 | 15·74 | 16·25 |
| Analysis, $CO_2$, per cent. | 3·20 | 4·75 | 6·00 | 6·60 | 7·00 | 7·35 | 8·05 | 8·10 | 7·85 | 7·65 | 1·20 |
| CO ,, | nil | 0·55 | 1·60 | 2·75 | 3·55 | 4·50 | 5·45 | 6·80 | 8·70 | 11·25 | 23·55 |
| "$C_xO_y$ *Gas.*" | | | | | | | | | | | |
| Volume, c.c. | 10·46 | 8·65 | 7·28 | 6·65 | 5·92 | 4·54 | 4·34 | 3·62 | 2·96 | 2·28 | 1·56 |
| Analysis, $CO_2$, per cent. | 18·45 | 15·35 | 11·45 | 8·40 | 7·65 | 7·05 | 4·15 | 3·65 | 2·20 | 0·80 | 0·15 |
| CO ,, | 81·20 | 84·40 | 88·20 | 86·10 | 90·05 | 91·05 | 95·35 | 95·95 | 97·55 | 99·05 | 99·70 |
| Percentage of oxygen burned appearing as: (1) $CO_2$ | 12·6 | 18·8 | 24·7 | 26·8 | 29·2 | 31·8 | 35·6 | 36·5 | 37·0 | 37·3 | 6·8 |
| (2) CO | — | 1·0 | 3·1 | 5·5 | 7·3 | 9·6 | 11·8 | 15·3 | 20·7 | 27·3 | 66·1 |
| (3) $C_xO_y$ | 87·4 | 80·2 | 72·2 | 67·7 | 63·5 | 58·6 | 52·6 | 48·2 | 42·3 | 35·6 | 27·1 |

The duration of heating in each experiment was a quarter of an hour. No oxygen could be detected in any of the samples of "Final Gas."

ture was raised from the experimental temperature to 1050° should be the same in each case, and that that rate should be rapid. This was effected by suddenly increasing the voltage of the current passing through the furnace to 200, maintaining that voltage until a temperature of about 1050° was reached, and then lowering it to 130. In this way the temperature of the furnace could be raised from 300° to 1050° in under ten minutes, and the latter temperature maintained without any serious fluctuations. The gas removed in this manner was measured and analysed as "$C_xO_y$ gas."

The results of the experiments are given in the table that follows. The volumes of "oxygen burned" are calculated from the total oxygen-content of the carbon dioxide and carbon monoxide in the "manometer," "final," and "$C_xO_y$" gases. All volumes are reduced to 0° and 760 mm. The duration of heating in each experiment was one hour.

At temperatures above 900° it was difficult to decide whether any oxygen became "fixed." Prolonged exhaustion at the experimental temperature continued to remove traces of gas until the whole of the oxygen admitted to the carbon could be accounted for as carbon dioxide and carbon monoxide. On the other hand, the last traces removed in this manner were very different in composition from the main bulk of the "final gas," and it seems likely that at temperatures above 900° reduction in pressure alone is sufficient to cause the decomposition of the complex.

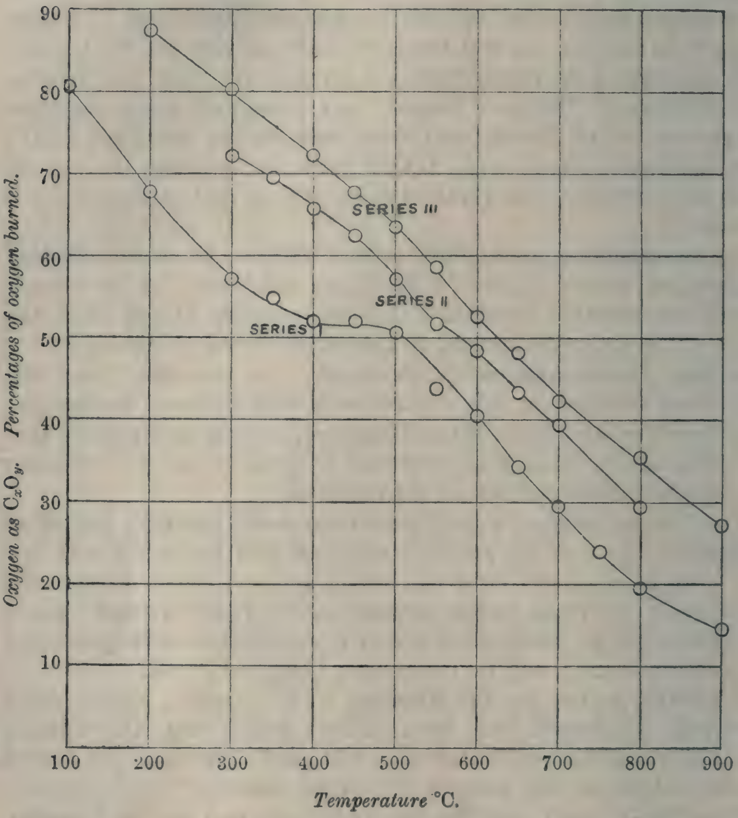
Two further series of experiments were made, one with a mixture of equal volumes of oxygen and nitrogen, and the other with air. The form of apparatus used was simplified for these two series, the gases being delivered under pressure to the reaction-vessel from a graduated holder (made from a 50 c.c. standard burette graduated in tenths of a c.c.), and no manometer being employed.

Although, owing to the dilution with nitrogen, rather small quantities of oxygen were used in each experiment, the volumes could be measured very accurately, and good agreement was always obtained between the volume of oxygen admitted to the carbon, as measured directly from the supply-burette, and the total oxygen-content of the "final gas" and the "$C_xO_y$ gas."

The curves in Fig. 4, prepared from the above three series of experiments, show the variation with temperature in the percentage of the oxygen burned that forms the complex $C_xO_y$, when a *limited* supply of oxygen is admitted to "exhausted" carbon.

When less oxygen is admitted to exhausted carbon than is sufficient to saturate it at the temperature employed, it becomes fixed very rapidly; and we imagine that *if no heating effect took place* all the oxygen admitted would become so fixed. A very slight increase in temperature is, however, sufficient to liberate some of the fixed oxygen as carbon dioxide and carbon monoxide. A certain proportion of the oxygen admitted, therefore, appears in the products of combustion as these gases. The percentage that thus appears depends on the heating effect produced; that is to say, it depends on the original temperature of the carbon and on the concentration of the oxygen.

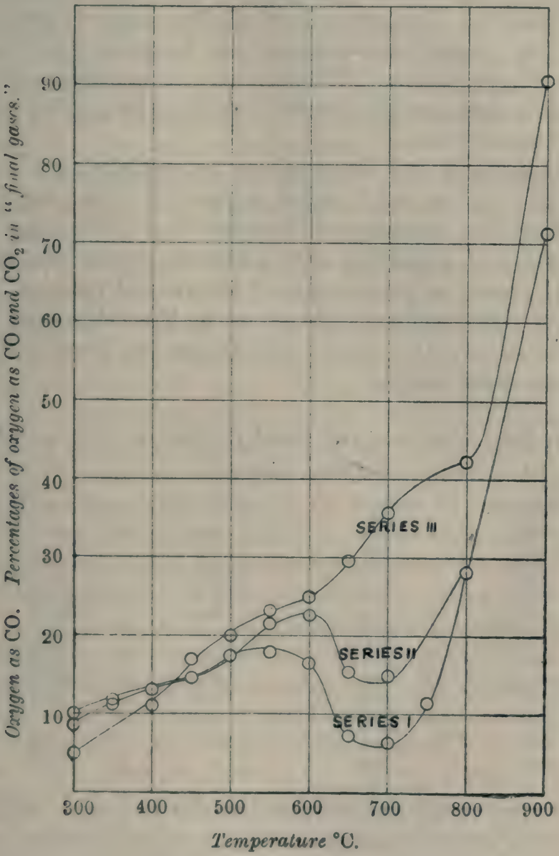
FIG. 4.



This is apparent on comparing the curves in Fig. 5. The smaller the concentration of the oxygen at any one temperature the larger the percentage of the oxygen burned that forms what we have assumed to be a physico-chemical complex, $C_xO_y$.

Taking the curve for pure oxygen (Series I), it will be seen that even at 900° as much as 14 per cent. of the oxygen burned forms the complex. The percentage does not increase regularly with decreasing temperature, but, when 500° is reached, remains fairly constant until 400°, after which the curve resumes its former inclination. Another similar series of experiments with pure oxygen (not recorded in this paper), in which the volume admitted was in excess of that required to saturate the carbon, showed a similar break in the curve for formation of $C_xO_y$ over the range

FIG. 5.



350—500°. The curve for "50 per cent." oxygen also shows a slight break at about 450°, that for air practically none.

We cannot at present assign any definite meaning to this break in the curve, unless it be that at temperatures between 400° and 500° the complex or series of complexes presumed to be formed have greater stability than at higher or lower temperatures. That it should appear but slightly defined in the curves for air and

50 per cent. oxygen is understandable for the reason that in these two series of experiments the volume of oxygen used was greatly in defect of that required for complete saturation of the carbon; whilst we have already seen that at all temperatures the *rate* of formation of the complex is about equally rapid; it is only the amount formed that varies.

Let us now turn our attention to the percentages of carbon dioxide and carbon monoxide produced apparently simultaneously with the complex. The percentage of the oxygen burned that appears as the gaseous oxides of carbon increases with increased temperature of the carbon. What we are more concerned with is the relationship between the amounts of these two oxides produced at different temperatures.

This relationship is best brought out by considering the oxygen-content of the "final gas," apart altogether from that of the complex. We have therefore calculated the percentages of the oxygen burned that appear as carbon dioxide and carbon monoxide in the "final gases" as percentages of the sum of the two.

The figures thus obtained are given in the table that follows, whilst Fig. 5 shows the curves for oxygen as carbon monoxide obtained from these figures.

*Oxygen as* CO. *Per cent. of Total Oxygen as* $CO_2$ *and* CO *in "Final Gases."*

| Temperature. | Series I. | Series II. | Series III. |
|---|---|---|---|
| 300° | 9·9 | 8·6 | 5·0 |
| 350 | 11·8 | 11·1 | — |
| 400 | 11·7 | 13·1 | 11·1 |
| 450 | 14·7 | 14·6 | 17·0 |
| 500 | 17·4 | 17·4 | 20·0 |
| 550 | 17·7 | 21·6 | 23·2 |
| 600 | 16·5 | 22·7 | 24·9 |
| 650 | 7·2 | 15·3 | 29·5 |
| 700 | 6·3 | 15·0 | 35·8 |
| 750 | 11·6 | — | — |
| 800 | 28·1 | 28·3 | 42·2 |
| 900 | 71·2 | — | 90·6 |

Taking the curve for pure oxygen (Series I) first, it will be seen that the percentage of the oxygen that appears as carbon monoxide increases fairly regularly until a temperature of about 550° is reached; it then decreases rapidly, to increase again at temperatures above 750°.

Until a temperature of 550° is attained the rate of the reaction $2CO + O_2 = 2CO_2$ is slow. Moreover, the occurrence of this reaction presumes the presence of an excess of oxygen for a certain length of time, whereas the volume of oxygen used in each experiment is in defect of that required for the formation of the total amount of the complex that can be formed with the weight of carbon used. Such oxidation of carbon monoxide molecules as takes place at these lower temperatures must therefore occur during the interval between the breaking up (owing to local heating) of some of the complex formed during the initial encounters between the oxygen molecules and the carbon, and the complete using up of the oxygen; a space of time which, owing to the rapidity of the reaction responsible for the formation of the complex, is not very great. Between 550° and 700°, however, the rate of oxidation of carbon monoxide rapidly increases, whilst the amount of oxygen rapidly removed to form the complex is not so great. A certain amount of carbon monoxide is thus capable of being oxidised before all the oxygen is removed from the sphere of action.

Finally, at temperatures above 750° the rate of the reaction $CO_2 + C = 2CO$ begins to be appreciable, and the quantity of carbon dioxide reduced at these higher temperatures depends largely, of course, on the length of time it is allowed to remain in contact with the carbon.

The curve for Series II (50 per cent. oxygen) is similar to that of Series I, but in this case a temperature of 600° has to be reached before the reaction $2CO + O_2 = 2CO_2$ begins to predominate.*

When air is used (Series III), the percentage of the oxygen burnt that appears as carbon monoxide in the final gases increases regularly up to 750° (when reduction of carbon dioxide begins to take place to an appreciable extent), no excess of oxygen being left sufficiently long at any temperature to oxidise the carbon monoxide to any great extent as it arises from decomposition of the complex.

It will be noticed that at temperatures below 450° the curve for the experiments with air passes beneath the curves for the series containing the larger percentages of oxygen. This is quite in accordance with the supposition that both the carbon dioxide and the carbon monoxide found in the "final gases" arise from decomposition of part of the complex first formed; for the decomposition when the higher concentrations of oxygen were present would take place at a slightly higher temperature—the encounters between

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* A series of experiments was made in a similar manner to the above with a mixture of carbon monoxide and oxygen containing 20 per cent. of carbon monoxide. The results showed that below 650° the rate of formation of carbon monoxide from the carbon was more rapid that the rate of oxidation of the carbon monoxide present in the original mixture; but that above that temperature the reverse was the case. Thus, the volumes of oxygen that entered the reaction-chamber as carbon monoxide, and the volumes found in the "final gases" were:

| Temperature. | 400° | 500° | 550° | 600° | 625° | 650° |
|---|---|---|---|---|---|---|
| Oxygen as CO in original gas, c.c. | 2·86 | 2·17 | 2·07 | 1·94 | 2·10 | 1·75 |
| Oxygen as CO in final gas, c.c. ... | 3·58 | 3·29 | 3·40 | 3·53 | 4·18 | 0·90 |
| Difference, c.c. ........................ | +0·72 | +1·12 | +1·33 | +1·59 | +2·18 | −0·85 |

the oxygen molecules and the carbon being more frequent—and we have shown that the higher the temperature of decomposition of the complex the lower the ratio $CO_2/CO$ in the gases evolved.

If our conception of what takes place is correct, these ratios $CO_2/CO$ in the experiments just recorded (Series III) should represent, at any rate for the lower temperatures, approximately the ratios in which the gases should make their appearance when a stream of air is passed over "saturated" carbon at corresponding temperatures. For we have shown that the volume of oxygen used in the experiments with air was so much in defect of that required to saturate the carbon, that the proportion of carbon monoxide found in the "final gases" can be regarded as having undergone but little diminution owing to oxidation by excess of oxygen; and that, therefore, the ratio in which carbon dioxide and carbon monoxide were found represents approximately at each temperature the ratio in which they arose from decomposition of the complex.

To put this hypothesis to the test, we have made a large number of experiments, in which "saturated" carbon was heated at different temperatures in streams of air and of oxygen at varying velocities. A sufficient number of data were obtained to enable us to eliminate the effects due to local heating of the carbon, or to subsequent interaction of the products of combustion and excess of either oxygen or carbon.

### *Experiments with "Saturated" Carbon.*

In distinguishing between exhausted and saturated carbon we have not intended to imply that there is any essential difference in their *mode* of combustion. The difference between what happens when oxygen is admitted to one or the other at a given temperature is, according to our hypothesis, simply that in the first case most of the oxygen molecules that encounter the carbon are permanently detained; whilst in the second case the detention is merely momentary. The exhausted carbon continues to detain oxygen molecules permanently until it becomes saturated.

In the experiments with *saturated* carbon at different temperatures now to be described dry air was drawn through the carbon, maintained at the experimental temperature, until the exit gases contained the proper oxygen-content for air. The carbon was then regarded as saturated at the experimental temperature. A measured volume of air (or oxygen) was then drawn at a constant speed through the carbon by means of a Sprengel mercury pump, and the whole of the products of combustion collected over mercury in a graduated reservoir. The "reaction-vessel" employed was a porcelain tube of 2 cm. internal diameter and 52 cm. long, into which a short, thin-walled tube of quartz containing the carbon just fitted, and was placed so as to occupy a central position.

Considerable difficulty was experienced in saturating the carbon and maintaining it saturated at the experimental temperature. Any accidental lowering in temperature after saturation had been completed rendered the carbon capable of causing the fixation of a further quantity of oxygen, and so caused a deficit in the oxygen-content of the issuing gases. It was found best, therefore, not to attempt to obtain as "experimental temperatures" for this series the even hundreds, 400°, 500°, etc., as had been done in previous series, but to get as near these values as possible by using a constant voltage of the electric current through the furnace, as near as possible to that which had previously been found to give the required temperature.

At temperatures above 550° a further difficulty arose in that the heat of the reaction caused a marked rise in the temperature of the carbon, and this rise in temperature was greater the more rapid the passage of the air current. To overcome this difficulty it was found necessary to continue the passage of the air-current at the velocity required for some little time before taking a sample of the issuing gases, the result being that for a given "experimental temperature" the *actual* temperature of the carbon varied with the velocity of the air-current.

The experimental temperature (as indicated by a thermo-couple embedded in the carbon) was measured at the outset of an experiment by the readings of a recording galvanometer giving a deflection of about 1 cm. per 100°. The "actual" temperatures were obtained during the course of the experiments from the deflection of a spot of light thrown by a "Broca" mirror galvanometer on a scale 40 cm. long. The resistance of the galvanometer was such that 3·66 millimetre divisions on the scale were equivalent to 1°. The zero of this instrument was set in each experiment at the "experimental temperature," so that the deflection observed showed at once the heating effect of the reaction.

As an example, to make the operation clear, we give the details of a series of experiments made at an experimental temperature of 640°. The carbon having been saturated at 640°, the first experiment of the series was made with a rapid current of air.

The velocity of the air-current was adjusted so as to be approximately 100 c.c. per minute. As soon as the stream was started the temperature of the carbon rose, the readings of the galvanometer being:

| Time, minutes. | Deflection of galvanometer. mm. | |
|---|---|---|
| 0 | 0 | "Experimental temperature," namely, 640°. |
| 1 | 52 | |
| 2 | 63 | |
| 3 | 68 | |
| 4 | 71 | |
| 5 | 72 | |
| 10 | 74 | = +20° |
| 15 | 74 | |
| 20 | 74 | The sample of the issuing gases was taken during this period. |
| 25 | 74 | |

The actual temperature was therefore 660°. The carbon was now allowed to regain the experimental temperature, and a stream of air of 100 c.c. in 2·3 minutes passed. A maximum deflection of the galvanometer equivalent to 37 mm. on the scale was produced. The "actual" temperature in this experiment was therefore 630°.

Similarly, with streams of 100 c.c. in 6·5 and 16·2 minutes the deflections observed were 4 mm. and 0 mm. respectively; the heating effect of the reaction could therefore be neglected in these two experiments.

In the table that follows each series of experiments is headed by the "experimental temperature." The "actual temperatures" are recorded in separate columns in each series. The other data given are:

(1) The number of the experiment, showing the order in which the different velocities of air-current were obtained. This is sometimes of importance when considering the general nature of the results of each series.

(2) The velocity of the air-current expressed as times of collection of 100 c.c.

(3) The analyses of the samples of the products of combustion.

(4) The ratios $CO_2/CO$ in the analyses.

(5) The proportions of the oxygen burned appearing as carbon monoxide.

(6) The percentage "oxygen-content" of the air burnt, calculated from the products of combustion. This should be about 20·9.

| Actual temperature. °C. | Expt. No. | Time of collection of 100 c.c. Mins. | Analysis, per cent. | | | Ratio $CO_2/CO$. | Oxygen as CO, per cent. of oxygen burned. | Oxygen-content of air. (Calculated) from the products of combustion. |
|---|---|---|---|---|---|---|---|---|
| | | | $CO_2$. | $O_2$. | CO. | | | |
| *Experimental Temperature* 400°. | | | | | | | | |
| 400 | 5 | 1·5 | 1·00 | 19·40 | 0·25 | 4·00 | 10·70 | 20·6 |
| 400 | 1 | 4·0 | 4·65 | 17·20 | 1·40 | 3·30 | 13·10 | 22·8 |
| 400 | 2 | 8·1 | 5·10 | 14·85 | 1·70 | 3·00 | 14·30 | 20·9 |
| 400 | 4 | 13·1 | 6·50 | 12·45 | 2·60 | 2·50 | 16·65 | 20·5 |
| 400 | | 14·7 | 7·50 | 11·30 | 3·30 | 2·25 | 18·05 | 20·8 |

| Actual temperature. °C. | Expt. No. | Time of collection of 100 c.c. Mins. | Analysis, per cent. $CO_2$. | $O_2$. | CO. | Ratio $CO_2/CO$. | Oxygen as CO, per cent. of oxygen burned. | Oxygen-content of air. (Calculated) from the products of combustion. |
|---|---|---|---|---|---|---|---|---|
| *Experimental Temperature* 425°. | | | | | | | | |
| 425 | 3 | 2·2 | 5·00 | 13·90 | 1·85 | 2·70 | 15·55 | 20·0 |
| 425 | 1 | 4·9 | 9·70 | 7·20 | 4·45 | 2·20 | 18·60 | 19·5 |
| 425 | 2 | 10·6 | 11·90 | 4·40 | 5·70 | 2·10 | 19·30 | 19·7 |
| 425 | 4 | 15·2 | 13·30 | 2·70 | 6·10 | 2·20 | 18·65 | 19·7 |
| *Experimental Temperature* 535°. | | | | | | | | |
| 560 | 1 | 2·7 | 14·10 | trace | 10·55 | 1·35 | 27·20 | 20·4 |
| 550 | 2 | 8·4 | 15·30 | nil | 9·85 | 1·55 | 24·30 | 20·4 |
| 545 | 3 | 12·0 | 15·55 | nil | 9·60 | 1·60 | 23·60 | 21·3 |
| 540 | 4 | 17·2 | 15·95 | nil | 9·85 | 1·60 | 23·60 | 21·6 |
| *Experimental Temperature* 570°. | | | | | | | | |
| 590 | 1 | 0·45 | 10·80 | 1·25 | 13·35 | 0·80 | 38·20 | 20·1 |
| 580 | 2 | 2·9 | 13·70 | nil | 13·05 | 1·05 | 32·25 | 21·6 |
| 575 | 3 | 8·0 | 15·25 | nil | 11·60 | 1·30 | 27·55 | 22·3 |
| 570 | 4 | 14·5 | 15·85 | nil | 10·00 | 1·60 | 24·00 | 21·9 |
| *Experimental Temperature* 600°. | | | | | | | | |
| 630 | 4 | 1·7 | 12·25 | nil | 15·80 | 0·80 | 39·20 | 21·8 |
| 610 | 2 | 7·9 | 14·05 | nil | 14·05 | 1·00 | 33·30 | 22·7 |
| 600 | 3 | 12·1 | 14·10 | nil | 12·95 | 1·10 | 31·45 | 22·0 |
| 600 | 1 | 23·4 | 15·85 | nil | 13·15 | 1·20 | 29·30 | 24·0 |
| *Experimental Temperature* 650°. | | | | | | | | |
| 680 | 1 | 1·4 | 11·70 | nil | 14·65 | 0·80 | 38·50 | 20·5 |
| 670 | 2 | 2·3 | 12·05 | nil | 13·60 | 0·90 | 36·05 | 21·0 |
| 655 | 3 | 6·5 | 13·10 | nil | 13·60 | 0·95 | 34·20 | 21·3 |
| 650 | 4 | 16·2 | 14·25 | nil | 11·80 | 1·20 | 29·30 | 21·4 |
| *Experimental Temperature* 700°. | | | | | | | | |
| 725 | 1 | 0·9 | 12·15 | trace | 13·90 | 0·90 | 36·30 | 20·6 |
| 710 | 3 | 4·2 | 14·20 | nil | 11·65 | 1·20 | 28·80 | 21·2 |
| 705 | 2 | 11·0 | 15·65 | nil | 8·75 | 1·80 | 21·60 | 20·9 |
| 705 | 4 | 21·0 | 16·70 | nil | 7·70 | 2·20 | 18·75 | 21·3 |
| *Experimental Temperature* 770°. | | | | | | | | |
| 780 | 1 | 1·3 | 19·00 | nil | 3·25 | 5·85 | 7·85 | 20·9 |
| 770 | 2 | 6·9 | 17·45 | nil | 5·70 | 3·05 | 14·00 | 20·9 |
| 770 | 3 | 14·5 | 17·50 | nil | 5·60 | 3·10 | 13·80 | 20·9 |
| 770 | 4 | 28·4 | 17·60 | nil | 4·60 | 3·80 | 11·55 | 20·4 |
| *Experimental Temperature* 840°. | | | | | | | | |
| 850 | 1 | 1·3 | 19·25 | nil | 2·80 | 6·90 | 6·80 | 20·9 |
| 845 | 2 | 5·3 | 19·10 | nil | 3·15 | 6·05 | 7·60 | 21·0 |
| 840 | 3 | 9·5 | 19·30 | nil | 2·90 | 6·65 | 7·00 | 21·0 |
| 840 | 4 | 25·0 | 19·40 | nil | 2·90 | 6·70 | 6·95 | 21·0 |
| *Experimental Temperature* 910°. | | | | | | | | |
| 915 | 1 | 0·8 | 18·85 | nil | 2·50 | 7·55 | 6·20 | 20·3 |
| 915 | 2 | 4·5 | 17·15 | nil | 5·00 | 3·45 | 12·70 | 20·2 |
| 910 | 3 | 13·7 | 16·30 | nil | 7·00 | 2·35 | 17·70 | 20·5 |
| 910 | 4 | 35·2 | 15·45 | nil | 8·50 | 1·80 | 21·55 | 20·6 |
| *Experimental Temperature* 1000°. | | | | | | | | |
| 1005 | 1 | 1·3 | 13·85 | nil | 11·35 | 1·20 | 29·80 | 20·1 |
| 1000 | 2 | 11·0 | 5·00 | nil | 25·00 | 0·20 | 71·55 | 20·0 |
| 1000 | 3 | 24·5 | 2·25 | nil | 29·95 | 0·05 | 86·95 | 20·3 |

These results considered together afford a very fair idea of the sequence of events when air is passed in a stream through heated carbon.* For their better comprehension the curves in Fig. 6

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* There are several points in connexion wiih these results which require explanation.

At 400° the ratio $CO_2/CO$ decreases regularly with decreasing speed of air-current. That is to say, the proportion of the oxygen burnt that appears as carbon monoxide is greater the slower the air-stream. This we presume to indicate the influence of local heating of the carbon. Any local heating would cause more rapid oxidation of carbon monoxide by excess of oxygen at those temperatures where excess of oxygen could remain in the gases for an appreciable time, namely, at temperatures below 500°. Its effects would be more apparent at those temperatures the more rapid the stream of air; for, as with the general heating effect, the local heating effect must be more intense the more rapid the air-current. In those experiments, therefore, where the general temperature of the carbon surface was insufficient to cause the *rapid* oxidation of carbon monoxide, a slow stream would yield a greater proportion of carbon monoxide than a fast stream. A very slow stream, or a slightly higher general temperature of the carbon, might occasion the oxidation of an appreciable quantity of carbon monoxide.

This contention is borne out by the results of the experiments at 425°, in which the proportion of the oxygen burnt that appears as carbon monoxide increases with decreasing rapidity of air-current up to a certain point, and then decreases. The explanation is that the slowest rate of passage of air in this series of experiments afforded time enough for the oxidation of carbon monoxide as it passed with excess of oxygen over the carbon surface, the general temperature of which was 425°.

At temperatures between 500° and 700° the ratio of $CO_2/CO$ in the products of combustion increases with decreasing velocity of air-current. At these temperatures the rate of oxidation of carbon monoxide is rapid, and the increased time of contact between the products of combustion (containing excess of oxygen) over the carbon surface afforded by slow streams, more than compensates for the diminution in the degree of local heating in its effect on the oxidation of carbon monoxide.

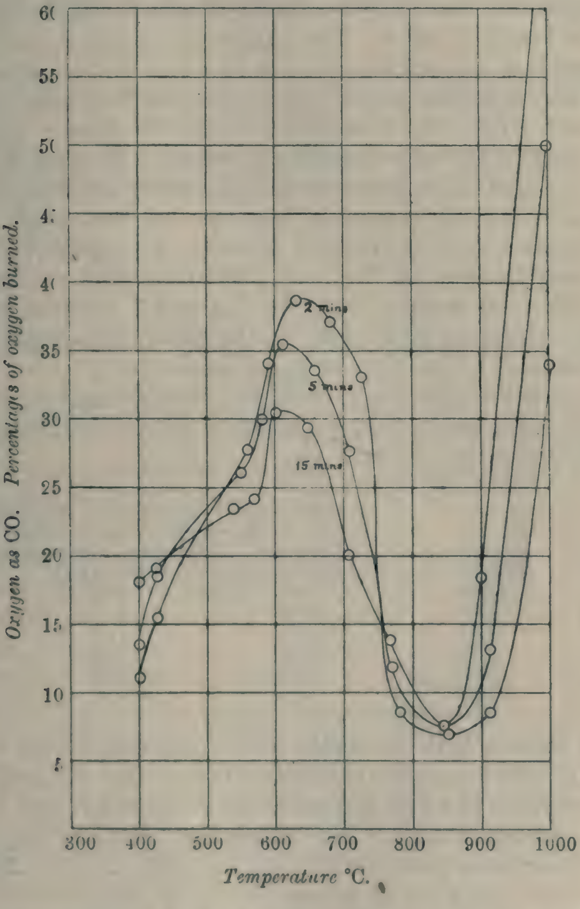
Above 850° the rate of the reaction $CO_2 + C = 2CO$ becomes appreciable, its effects being, as might be expected, more marked the slower the stream of air. It is interesting to note that even with the slowest stream at 1000° equilibrium of the system $2CO \rightleftharpoons CO_2 + C$ was not attained.

We may remark that all these results have been confirmed by duplicate series of experiments.

There is a further point in connexion with these experiments to which attention should be drawn, namely, the variations in the oxygen-content of the products of combustion. Allowing for the increase in volume due to the formation of carbon monoxide, the oxygen-content of the original air passed can be calculated. It should be about 20·9. The fact that in many cases a greater and in some cases a smaller percentage was found emphasises what we have already said regarding the difficulty of maintaining the carbon "saturated" at the experimental temperature. We are satisfied that the fluctuations in the oxygen-contents observed are not due to experimental error—we believe that the determinations of the constituents of the products of combustion are correct within 0·05 per cent.—and it will be observed that there is a certain regularity amongst them, each series at a particular experimental temperature yielding a uniformly high or low result as the case may be. The high results we attribute to excessive decomposition of the complex, due to the heat of the reaction; the low results to insufficient saturation of the carbon before collection of the samples was made.

have been plotted. These curves represent the percentages of the oxygen burnt that appear in the products of combustion as carbon monoxide at different temperatures, with speeds of air-current yielding 100 c.c. in 2, 5, and 15 minutes respectively. The percentages for these speeds are interpolated from the experimental numbers, the temperatures being to the nearest 5 degrees.

FIG. 6.



The temperatures at which the reactions $2CO + O_2 = 2CO_2$ and $CO_2 + C = 2CO$ are most prominent can readily be seen from these curves. We are most concerned, however, with the curve for temperatures below 650°, at which temperature the percentage of oxygen as carbon monoxide reaches its maximum with the most rapid air-current; for below this temperature, with rapid air-currents, the effects of reactions subsequent to the oxidation of carbon do not predominate.

If from the curve for the most rapid air-current the percentages of oxygen as carbon monoxide at temperatures of 400°, 450°, 500°, 550°, 600°, and 650° be taken, the ratio $CO_2/CO$ in the products of combustion at these temperatures can be calculated, and comparison made with the ratios obtained in the "fixation" experiments with air. In these latter experiments, it will be remembered, it was concluded that the percentages of carbon dioxide and carbon monoxide found at the end of a quarter of an hour's heating could be regarded as approximately those in which the gases were liberated by decomposition of the complex, at any rate at temperatures below 500°. For at these temperatures the small quantity of oxygen used in the experiments was removed so quickly from the sphere of action as to preclude the possibility of much secondary oxidation of carbon monoxide, the rate of that reaction being slow. Between 500° and 700°, however, it appeared probable, from a consideration of the results obtained from similar experiments with pure oxygen and "50 per cent." oxygen, that some secondary oxidation took place in the time. The ratio $CO_2/CO$ would therefore be too high at these temperatures.

We give below the results obtained for the ratio in the rapid "stream" experiments just described, together with those in the "fixation" experiments with air:

| | Ratio $CO_2/CO$ in products of combustion. | |
|---|---|---|
| Temperature. | "Stream" experiments. | "Fixation" experiments. (Series III.) |
| 400° | 3·80 | 3·75 |
| 450 | 2·28 | 2·40 |
| 500 | 1·70 | 1·97 |
| 550 | 1·35 | 1·63 |
| 600 | 0·90 | 1·48 |
| 650 | 0·78 | 1·19 |

It will be seen that the results are of the same order, the ratio decreasing with increasing temperature; and that at temperatures below 550° there is a fair agreement between the two sets of ratios. Above that temperature, as anticipated, the "fixation" experiments show a higher ratio than the "stream" experiments, due, no doubt, to subsequent oxidation of carbon monoxide, the extent of which would be minimised in the rapid stream experiments.

On the one hand, therefore, we have a set of ratios $CO_2/CO$ in the products of combustion obtained during the oxidation of "saturated" or "normal" carbon in a stream of air; and on the other hand a similar set of ratios obtained during the "fixation" of oxygen by "exhausted" carbon, when the major portion of the oxygen burnt is retained by the carbon to form (presumably) a carbon–oxygen complex, such oxygen as appears in the gaseous products of combustion being due to the decomposition of this complex. The two sets of ratios show considerable concordance. The hypothesis is that in the normal burning of carbon the carbon dioxide and carbon monoxide found as the apparently primary products of combustion arise from the decomposition, at the temperature of combustion, of a complex, the formation of which is the first result of the encounters between oxygen and carbon molecules.

Our thanks are due to the Explosions in Mines Committee of the Home Office for permission to publish these results.

We wish, also, to express our appreciation of Professor Bone's kindness in communicating this paper to the Society.

ESKMEALS.

# LIV.—*Existence of Racemic Compounds in the Liquid State.*

By ALEC DUNCAN MITCHELL and CLARENCE SMITH.

DURING the past twenty years various physical properties of liquids have been utilised in an attack on the problem of the existence of racemic compounds in the liquid state, but the change of the molecular surface energy with temperature appears not to have been applied until Gróh a few months ago (*Ber.*, 1912, **45**, 1441) recorded the result of two experiments on dimethyl tartrate and dimethyl racemate.

A survey of the results obtained by different investigators, a summary of which can be found in recent papers on this subject by Dunstan and Thole (T., 1908, **93**, 1815; 1910, **97**, 1249; this vol., p. 19) leaves on the mind the impression that the existence in the liquid state of a racemic compound of two enantio-stereoisomerides has not been definitely and satisfactorily established. Several investigators assert that liquid racemates do exist, but the weight such statements carry is a matter of opinion, in view of the uncertain quantitative value of most of the methods by which the problem has been treated. Methods based on the determination of the density or of the refractive index (Traube, *Ber.*, 1896, **29**, 1394; Pope and Peachey, T., 1899, **75**, 1111), by which therefore the greatest accuracy can be attained, definitely deny the existence of racemic compounds in unassociated liquids.

Ramsay and Shields have shown (*Phil. Trans.*, 1893, **184**, 647) how the molecular weight of a pure unassociated liquid can be determined from the rate of change of the molecular surface energy with temperature; for such liquids the relation between the change and the temperature is linear, except in the neighbourhood of the critical point, and the rate of change is a constant, $k$, the average value of which, determined by six "normal" liquids, is 2·1209. Before the application of this method to the problem of the existence of liquid racemates is described, some discussion of the significance of the constant $k$ is necessary. The average value, 2·1209, is the mean of six lying between 2·2256 for ethyl acetate and 2·0419 for methyl formate. Values even greater than the former have been recorded in recent years by Hewitt and Winmill (T., 1907, **91**, 441), Turner and Merry (*ibid.*, 1910, **97**, 2069), Walden and Swinne (*Zeitsch. physikal. Chem.*, 1912, **79**, 700), and others. The criterion of the unaltered molecular complexity of a liquid with change of temperature is not so much the absolute value of $k$, as its constancy. When the liquid is unassociated, $k$ remains the same over a wide range of temperature, but in the case of an associated liquid the dissociation which accompanies rise of temperature is manifested by a rapid increase in the value of $k$. Thus, for ethyl alcohol and for glacial acetic acid, $k$ has the values 1·070 and 0·8815 respectively at 20° and 1·569 and 1·198 respectively at 150°.

The application of this method to the problem under examination is as follows. The surface tensions and the densities of each of the optically active modifications of a substance are determined over as wide a range of temperature as is practically convenient, and thereby, assuming a normal molecular weight for the substance, several values of $k$ are obtained by the equation

$$k = \frac{\delta[\gamma(Mv)^{\frac{2}{3}}]}{\delta t},$$

and the mean is calculated.

The same measurements are made with the inactive modification, and the mean value of $k'$ is determined, again assuming a normal molecular weight for the substance. If this assumption is correct, that is, if the inactive modification is a liquid mixture of the two active forms, the mean values of $k$ and $k'$ will be identical or nearly so. On the other hand, if the inactive substance is a liquid racemic compound, and therefore has twice the molecular weight of the active modifications, $k'$ will be smaller than $k$, the two quantities being related by the equation $k = 2^{\frac{2}{3}}k'$. Finally, the inactive liquid may be a mixture of the two active forms in equilibrium with the racemic compound. In this case $k$ will the more exceed $k'$ the greater the amount of the racemic compound present, a change of

0·01 in the value of $k'$ corresponding roughly with a change of about 0·7 per cent. in the molecular weight. (Strictly speaking, the name "molecular weight" is inapplicable to such a liquid; its meaning, however, is obvious, and the name will be retained to avoid circumlocution.)

There remains to be considered the question of the association, other than the chemical combination, of the liquid molecules. This complication has been avoided by selecting for examination substances which the experience of previous workers has shown are little prone to association, namely, hydrocarbons and esters. The active and the inactive modifications of pinene and of limonene, and dimethyl *d*-tartrate and dimethyl racemate have been examined. The concordant values of $k$ for the active and the inactive modifications of each substance and its constancy over a wide range of temperature prove that the substances selected fulfilled expectation, and that the results are not complicated by changes due to ordinary association.

## EXPERIMENTAL.

The apparatus and the general mode of procedure for the determinations of the surface tension at different temperatures were similar to those described by Hewitt and Winmill (*loc. cit.*). All measurements of length were made with a vernier microscope reading directly to 0·01 mm., and by means of a micrometer eyepiece to 0·001 mm. Many capillary tubes were tested until one was found with a uniform bore over a length of 5—6 cm. This was then sealed to the wide tube of the apparatus, so that the surface of the liquid within the capillary was always situated within the uniform portion. The usual precautions were observed of thoroughly wetting the capillary walls and of determining the surface tension of the liquid in contact with its own vapour. The diameter of the uniform part of the capillary tube was determined by direct measurement with the micrometer eye-piece, by calibration with a mercury thread, and by a determination of the surface tension of benzene; the three methods gave practically identical results.

The densities of the liquids at different temperatures were determined by means of a dilatometer consisting of a cylindrical bulb of about 9 c.c. capacity sealed to a capillary tube, in which six or seven small bulbs, of about 0·04 c.c. capacity, were blown at intervals of about 2·5 cm. File marks were made on the capillary stem between the small bulbs. The dilatometer with the bulb completely filled with the liquid under examination was immersed in a large bath of water or other liquid heated by a small flame.

The temperatures to 0·1° were noted at which the liquid surface coincided with the various file marks on the capillary stem. The dilatometer was calibrated by a series of readings with water. This method of determining the densities of a liquid at different temperatures was devised by Mr. T. F. Winmill. It is very convenient and accurate. After the densities of benzene at different temperatures between 15° and 75° had been determined, it was found that the results agreed to 0·0001 with those obtained by Walden (*Zeitsch. physikal. Chem.*, 1909, **65**, 129).

The values of *h* recorded are obtained from smoothed curves of the experimental values.

### *Pinene.*

d-*Pinene.*—The liquid, after repeated fractionation under diminished pressure, boiled at 85°/80 mm., and had $[\alpha]_D^{15}$ 13·4°.

l-*Pinene.*—Purified in a similar manner. Boiling point 70·5°/35 mm.; $[\alpha]_D^{15}$ $-22·0°$.

i-*Pinene.*—Sample I. Prepared from pinene nitrosochloride by Wallach's method. Boiling point 156°. Optically inactive. In the experiments, it became slightly yellow after keeping for some time at the higher temperatures, but after cooling, the surface tension was found to be unchanged.

Sample II. Prepared by mixing *d*- and *l*-pinenes to produce an optically inactive liquid.

d-*Pinene.* M = 136. *r* = 0·02790.

| *t.* | *d.* | *h.* | *γ.* | $\gamma(Mv)^{\frac{2}{3}}$. | | $k_{(12·6-t)}$. |
|---|---|---|---|---|---|---|
| 12·6 | 0·8686 | 2·292 | 27·23 | 790·9 | $k_{(12·6-62·0)}$ = 2·38 | — |
| 23·8 | 0·8592 | 2·222 | 26·11 | 764·0 | | 2·40 |
| 35·9 | 0·8491 | 2·146 | 24·93 | 735·4 | $k_{(23·8-71·0)}$ = 2·37 | 2·38 |
| 49·8 | 0·8378 | 2·058 | 23·60 | 702·3 | | 2·38 |
| 62·0 | 0·8277 | 1·983 | 22·45 | 673·4 | $k_{(35·9-82·5)}$ = 2·35 | 2·38 |
| 71·0 | 0·8202 | 1·927 | 21·61 | 652·1 | | 2·38 |
| 82·5 | 0·8106 | 1·856 | 20·58 | 625·9 | $k_{(49·8-91·4)}$ = 2·33 | 2·36 |
| 91·4 | 0·8032 | 1·801 | 19·79 | 605·5 | | 2·35 |
| | | | | | Mean = 2·36 | 2·37 |

l-*Pinene.* M = 136. *r* = 0·02790.

| *t.* | *d.* | *h.* | *γ.* | $\gamma(Mv)^{\frac{2}{3}}$. | | $k_{(11·4-t)}$. |
|---|---|---|---|---|---|---|
| 11·4 | 0·8709 | 2·290 | 27·27 | 790·8 | $k_{(11·4-58·8)}$ = 2·36 | — |
| 20·9 | 0·8630 | 2·229 | 26·32 | 767·7 | | 2·43 |
| 34·3 | 0·8519 | 2·147 | 25·03 | 736·3 | $k_{(20·9-69·7)}$ = 2·33 | 2·38 |
| 47·7 | 0·8410 | 2·064 | 23·74 | 704·6 | | 2·37 |
| 58·8 | 0·8317 | 1·996 | 22·71 | 679·0 | $k_{(34·3-79·7)}$ = 2·33 | 2·36 |
| 69·7 | 0·8226 | 1·929 | 21·70 | 654·0 | | 2·35 |
| 79·7 | 0·8143 | 1·868 | 20·81 | 630·8 | $k_{(47·7-93·8)}$ = 2·26 | 2·34 |
| 93·8 | 0·8025 | 1·786 | 19·61 | 600·3 | | 2·31 |
| | | | | | Mean = 2·32 | 2·36 |

i-*Pinene* (sample I). M = 136. $r = 0·02790$.

| $t$. | $d$. | $h$. | $\gamma$. | $\gamma(Mv)^{2/3}$. | | $k_{(32·6-t)}$. |
|---|---|---|---|---|---|---|
| 32·6 | 0·8513 | 2·124 | 24·73 | 728·1 | $k_{(32·6-77·8)} = 2·38$ | — |
| 35·6 | 0·8488 | 2·105 | 24·43 | 720·5 | | — |
| 49·2 | 0·8377 | 2·019 | 23·13 | 688·2 | $k_{(35·6-88·0)} = 2·32$ | 2·40 |
| 61·4 | 0·8275 | 1·941 | 21·96 | 658·9 | | 2·40 |
| 63·2 | 0·8260 | 1·930 | 21·80 | 655·1 | $k_{(49·2-93·8)} = 2·36$ | 2·39 |
| 77·8 | 0·8139 | 1·837 | 20·45 | 620·4 | | 2·38 |
| 88·0 | 0·8054 | 1·775 | 19·60 | 598·9 | $k_{(61·4-95·0)} = 2·33$ | 2·33 |
| 93·8 | 0·8003 | 1·738 | 19·00 | 582·9 | | 2·37 |
| 95·0 | 0·7994 | 1·731 | 18·91 | 580·5 | | 2·37 |
| | | | | | Mean = 2·35 | 2·38 |

i-*Pinene* (sample II). M = 136. $r = 0·04823$.

| $t$. | $d$. | $h$. | $\gamma$. | $\gamma(Mv)^{2/3}$. | | $k_{(8·6-t)}$. |
|---|---|---|---|---|---|---|
| 8·6 | 0·8725 | 1·318 | 27·22 | 788·0 | $k_{(8·6-42·2)} = 2·34$ | — |
| 9·3 | 0·8719 | 1·317 | 27·17 | 787·2 | | [1·14] |
| 11·7 | 0·8699 | 1·307 | 26·86 | 780·5 | $k_{(9·3-59·5)} = 2·36$ | 2·42 |
| 23·9 | 0·8598 | 1·264 | 25·64 | 752·1 | | 2·35 |
| 42·2 | 0·8446 | 1·199 | 23·96 | 709·3 | $k_{(11·7-73·0)} = 2·33$ | 2·34 |
| 59·5 | 0·8305 | 1·137 | 22·34 | 668·6 | | 2·35 |
| 73·0 | 0·8192 | 1·089 | 21·15 | 637·7 | $k_{(23·9-88·3)} = 2·30$ | 2·33 |
| 88·3 | 0·8073 | 1·037 | 19·82 | 604·1 | | 2·31 |
| | | | | | Mean = 2·33 | 2·35 |

## *Limonene.*

d-*Limonene.*—Purified by repeated distillation under diminished pressure. Boiling point 135°/240 mm.; $[\alpha]_D^{15}$ 122·6°.

l-*Limonene.*—Purified in a similar manner. Boiling point 100°/73 mm.; $[\alpha]_D^{15}$ − 105·4°.

i-*Limonene.*—(Dipentene). Sample I. Repeatedly distilled. Boiling point 176°/760 mm.

Sample II. By mixing *d*- and *l*-limonenes to produce an inactive liquid.

d-*Limonene.* M = 136. $r = 0·04823$.

| $t$. | $d$. | $h$. | $\gamma$. | $\gamma(Mv)^{2/3}$. | | $k_{(10·9-t)}$. |
|---|---|---|---|---|---|---|
| 10·9 | 0·8511 | 1·417 | 28·53 | 840·0 | $k_{(10·9-58·4)} = 2·35$ | — |
| 23·1 | 0·8413 | 1·372 | 27·31 | 810·1 | | 2·45 |
| 34·2 | 0·8329 | 1·334 | 26·41 | 788·9 | $k_{(23·1-70·7)} = 2·31$ | 2·19 |
| 44·4 | 0·8247 | 1·297 | 25·31 | 761·0 | | 2·36 |
| 58·4 | 0·8138 | 1·247 | 24·00 | 728·4 | $k_{(34·2-85·6)} = 2·39$ | 2·35 |
| 70·7 | 0·8044 | 1·203 | 22·90 | 700·2 | | 2·34 |
| 85·6 | 0·7927 | 1·150 | 21·57 | 665·9 | $k_{(44·4-90·3)} = 2·30$ | 2·33 |
| 90·3 | 0·7892 | 1·133 | 21·16 | 655·2 | | 2·33 |
| | | | | | Mean = 2·34 | 2·335 |

l-*Limonene.* M = 136. $r = 0·04823$.

| $t$. | $d$. | $h$. | $\gamma$. | $\gamma(Mv)^{2/3}$. | | $k_{(6·2-t)}$. |
|---|---|---|---|---|---|---|
| 6·2 | 0·8600 | 1·400 | 28·48 | 832·7 | $k_{(6·2-57·1)} = 2·25$ | — |
| 23·2 | 0·8464 | 1·342 | 26·87 | 794·1 | | 2·27 |
| 35·4 | 0·8368 | 1·300 | 25·73 | 766·2 | $k_{(23·2-71·2)} = 2·23$ | 2·28 |
| 45·1 | 0·8291 | 1·267 | 24·85 | 744·6 | | 2·26 |
| 57·1 | 0·8197 | 1·226 | 23·78 | 718·0 | $k_{(35·4-82·1)} = 2·23$ | 2·25 |
| 71·2 | 0·8085 | 1·179 | 22·55 | 687·3 | | 2·24 |
| 82·1 | 0·7999 | 1·140 | 21·56 | 662·0 | $k_{(45·1-95·5)} = 2·20$ | 2·25 |
| 95·5 | 0·7895 | 1·096 | 20·48 | 633·9 | | 2·23 |
| | | | | | Mean = 2·23 | 2·25 |

*i-Limonene* (sample I). M = 136. $r = 0·04823$.

| $t$. | $d$. | $h$. | $\gamma$. | $\gamma(Mv)^{\frac{2}{3}}$. | | $k_{(10·5-t)}$. |
|---|---|---|---|---|---|---|
| 10·5 | 0·8668 | 1·366 | 28·00 | 814·7 | $k_{(10·5-57·1)} = 2·30$ | — |
| 22·8 | 0·8570 | 1·322 | 26·80 | 785·5 | | 2·38 |
| 34·6 | 0·8475 | 1·282 | 25·12 | 759·1 | $k_{(22·8-69·9)} = 2·26$ | 2·31 |
| 45·1 | 0·8393 | 1·245 | 24·72 | 734·6 | | 2·32 |
| 57·1 | 0·8296 | 1·204 | 23·63 | 707·8 | $k_{(34·6-81·7)} = 2·25$ | 2·30 |
| 69·9 | 0·8195 | 1·160 | 22·50 | 679·1 | | 2·29 |
| 81·7 | 0·8100 | 1·120 | 21·46 | 653·1 | $k_{(45·1-93·8)} = 2·24$ | 2·27 |
| 93·8 | 0·8004 | 1·077 | 20·40 | 625·7 | | 2·27 |
| | | | | | Mean = 2·26 | 2·29 |

i-*Limonene* (sample II). M = 136. $r = 0·04823$.

| $t$. | $d$. | $h$. | $\gamma$. | $\gamma(Mv)^{\frac{2}{3}}$. | | $k_{(10·8-t)}$. |
|---|---|---|---|---|---|---|
| 10·8 | 0·8538 | 1·397 | 28·22 | 829·1 | $k_{(10·8-57·2)} = 2·33$ | — |
| 24·2 | 0·8432 | 1·349 | 26·90 | 797·1 | | 2·39 |
| 35·0 | 0·8348 | 1·311 | 25·89 | 772·3 | $k_{(24·2-69·6)} = 2·29$ | 2·35 |
| 46·6 | 0·8247 | 1·270 | 24·78 | 745·0 | | 2·35 |
| 57·2 | 0·8174 | 1·233 | 23·84 | 721·1 | $k_{(35·0-81·7)} = 2·29$ | 2·33 |
| 69·6 | 0·8076 | 1·190 | 22·73 | 693·3 | | 2·31 |
| 81·7 | 0·7981 | 1·147 | 21·65 | 665·6 | $k_{(46·6-96·2)} = 2·26$ | 2·31 |
| 96·2 | 0·7868 | 1·096 | 20·40 | 633·1 | | 2·30 |
| | | | | | Mean = 2·29 | 2·33 |

*Dimethyl* d-*Tartrate*.—Repeatedly fractionated under low pressure. The sample employed boiled at 158°/13 mm., melted at 42·4°, and had $[\alpha]_{\mathrm{D}}^{15}$ − 9·2° (5 per cent. solution in chloroform).

*Dimethyl Racemate*.—Purified by distillation under diminished pressure. Boiling point 169°/20 mm.; melting point, 89·5°.

*Methyl* d-*Tartrate*. M = 178. $r = 0·04823$.

| $t$. | $d$. | $h$. | $\gamma$. | $\gamma(Mv)^{\frac{2}{3}}$. | | $k_{((62·0-t)}$. |
|---|---|---|---|---|---|---|
| 62·0 | 1·2903 | 1·278 | 39·02 | 1042·0 | $k_{(62·0-100·0)} = 2·04$ | — |
| 62·6 | 1·2896 | 1·276 | 38·94 | 1040·0 | | [3·33] |
| 67·2 | 1·2850 | 1·267 | 38·52 | 1031·5 | $k_{(62·6-124·0)} = 1·98$ | 2·02 |
| 96·3 | 1·2545 | 1·204 | 35·72 | 972·0 | | 2·04 |
| 100·0 | 1·2506 | 1·196 | 35·39 | 964·6 | $k_{(67·2-126·0)} = 1·99$ | 2·04 |
| 124·0 | 1·2255 | 1·146 | 33·23 | 918·2 | | 2·00 |
| 126·0 | 1·2235 | 1·142 | 33·06 | 914·6 | $k_{(96·3-135·1)} = 1·96$ | 1·99 |
| 135·1 | 1·2140 | 1·122 | 32·22 | 896·0 | | 2·00 |
| | | | | | Mean = 1·99 | 2·015 |

*Methyl Racemate*. M = 178. $r = 0·04823$.

| $t$. | $d$. | $h$. | $\gamma$. | $\gamma(Mv)^{\frac{2}{3}}$. | | $k_{(89·6-t)}$. |
|---|---|---|---|---|---|---|
| 89·6 | 1·2604 | 1·181 | 35·22 | 955·2 | $k_{(89·6-150·6)} = 2·04$ | — |
| 92·5 | 1·2575 | 1·174 | 34·93 | 948·6 | | [2·28] |
| 103·6 | 1·2458 | 1·149 | 33·86 | 925·6 | $k_{(92·5-157·4)} = 2·03$ | 2·11 |
| 124·8 | 1·2237 | 1·103 | 31·93 | 883·0 | | 2·05 |
| 150·6 | 1·1968 | 1·045 | 29·59 | 830·5 | $k_{(103·6-159·0)} = 2·01$ | 2·04 |
| 157·4 | 1·1897 | 1·030 | 28·99 | 817·0 | | 2·04 |
| 159·0 | 1·1880 | 1·027 | 28·86 | 814·1 | $k_{(124·8-159·2)} = 2·03$ | 2·03 |
| 159·2 | 1·1878 | 1·026 | 28·83 | 813·3 | | 2·04 |
| | | | | | Mean = 2·03 | 2·05 |

A comparison of the mean values of $k$, which are tabulated separately for convenience of reference, obtained with each set of liquids, shows that the active and the inactive modifications in each case have the same degree of molecular complexity, and, therefore, that the inactive modifications are not racemic compounds.

The last column in each table gives the values of $k$ calculated from the molecular surface energies at the lowest temperature and each succeeding temperature. The mean value in the last column agrees with the mean value obtained at approximately equal intervals of temperature over the whole range. The values in brackets have not been taken into account, being calculated from temperature differences too small to give accurate results. The individual values of $k$ in the last column decrease slightly and fairly uniformly with rise of temperature. This cannot be taken as evidence of racemate formation, because the change occurs both with the active and inactive modifications. Neither can it be due to association, because no evidence has ever been placed on record of association being accompanied by an absorption of heat. It must be attributed to some unknown factor which is operating both in the active and the inactive modifications of the substance.

The case of the methyl esters of active and inactive tartaric acids is interesting. Our values of $k$ are 1·99 and 2·03 respectively, corresponding with association factors ($x$) of 1·10 and 1·07. In the paper already referred to, Gróh obtains the values 2·37 and 2·26 respectively, corresponding with $x=0·85$ and 0·91. It is, presumably, in view of the latter value that he concludes that the inactive form is unimolecular and not racemic; but by comparison with the value (0·85) for the active ester he would apparently have been justified in indicating slight molecular complexity for the racemate. Our results point to an anomalous state, the tartrate ($x=1·10$) being more associated than the racemate. From these figures it appears that racemates have no existence in the liquid state:

| | $k$. | $k'$. |
|---|---|---|
| *d*-Pinene | 2·36 | 2·37 |
| *l*-Pinene | 2·32 | 2·36 |
| *i*-Pinene (sample I.) | 2·35 | 2·38 |
| ,, (sample II.) | 2·33 | 2·35 |
| *d*-Limonene | 2·34 | 3·335 |
| *l*-Limonene | 2·23 | 2·25 |
| *i*-Limonene (sample I.) | 2·26 | 2·29 |
| ,, (sample II.) | 2·29 | 2·33 |
| Dimethyl-*d*-tartrate | 1·99 | 2·015 |
| Dimethyl racemate | 2·03 | 2·05 |

In conclusion, we wish to express our thanks to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

East London College.

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# LV.—*The Interaction of Chlorine and Hydrogen. The Influence of Mass.*

By David Leonard Chapman and Leo Kingsley Underhill.

When the conditions are such that a chemical change in a system can take place only under the influence of light, the velocity of the change is known to be proportional to the light absorbed by the coloured constituents of the system in unit time, provided that the character of the light and the composition of the system be fixed. If the light be monochromatic and the composition of the system be variable, the velocity of chemical change will be given by the numerical value of an expression of the form:

$$k_n E_n f_n(c_1, c_2 \ldots .),$$

in which $E_n$ is the light energy, of frequency $n$, absorbed in unit time, $k_n$ is a number the value of which depends on the vibration frequency, and $f_n(c_1, c_2 \ldots .)$ is an unknown function of $c_1$, $c_2$, etc., the concentration of the constituents of the mixture, and possibly also of $n$.* It it be assumed that the function in question is independent of the vibration frequency of the light, the rate of chemical change in a system illuminated by composite light would be given by the expression:

$$f(c_1, c_2 \ldots )\int k_n \frac{dE_n}{dn} dn,$$

the limits of the integral being the maximum and minimum values of the vibration frequencies of the composite light.

In order to determine experimentally the nature of the function $f$ the value of the integral $\int k_n \frac{dE_n}{dn} dn$ must during the course of the experiment be determinable at any moment, or be constant. By preference it should be maintained constant.

Unfortunately, in several investigations that have been undertaken with the object of estimating the influence of mass on photochemical changes the energy integral was not maintained constant, nor was any attempt made to estimate and to introduce a correction for its variation during the course of the reaction. M. Wilderman's experiments (*Phil. Trans.*, 1902, **199**, 337) on the interaction of carbon monoxide and chlorine, for example, were vitiated by this source of error. Mixtures of carbon monoxide and chlorine enclosed in a vessel of 3·5 cm. diameter were exposed to light, and the rates of union of the gases, determined from readings of the variations in pressure, taken at stated intervals of time, the readings being continued until a considerable proportion of the chlorine originally present had disappeared. Under such conditions the light absorbed must have diminished considerably during the progress of the experiment, and the conclusion drawn by Wilderman from his uncorrected measurements, namely, that the chemical change in question is bimolecular, and conforms to the same law of mass as a purely idiochemical change, cannot therefore be accepted as valid. Strictly, his experiments can be taken only to indicate that, under conditions which would secure a constant rate of absorption of light, the order of the change would be lower than the second.

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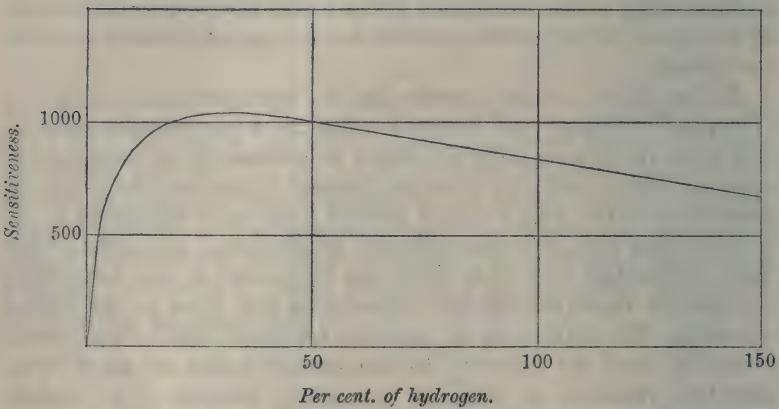
* It is probable, but by no means certain, that $f$ is independent of $n$. It has been invariably assumed that such is the case, although the published experimental evidence which supports the assumption is not entirely satisfactory.

At first sight it might appear that the photochemical interaction of carbon monoxide and chlorine would be a particularly suitable change to investigate with the object of estimating the influence of mass on the velocity of a photochemical transformation; but in practice we have found that a serious obstacle is presented to its investigation owing to the difficulty of obtaining mixtures of the gases containing only such inhibitive impurities as are not slowly changed or destroyed by the influence of the light as the action proceeds. The impurities in question are contained in the carbon monoxide, and we have up to the present failed to effect their complete removal, in spite of numerous attempts by various methods. Accordingly we have had to fall back on the action between chlorine and hydrogen. Although the rate of interaction between these gases cannot be measured with such ease as that between chlorine and carbon monoxide, yet the mixture can, with the exception of oxygen (which does not alter in amount under the influence of light), be obtained uncontaminated with impurities which retard the change.

Our object has been to investigate, in the first place, the influence of the concentration of the hydrogen on the rate of formation of hydrogen chloride. The partial pressures of the chlorine and of the oxygen in the mixtures examined in one series of experiments were therefore kept constant, whereas that of the hydrogen was varied. A small amount of oxygen was added to the chlorine in order to make it quite certain that the mixtures rich in hydrogen did not contain an appreciably larger proportion of oxygen than those poorer in hydrogen, as would otherwise have been the case if the hydrogen had adventitiously, or as a result of its method of preparation, contained a trace of oxygen. The intensity of illumination was always the same, and, as the concentration of the chlorine was also invariable, the energy absorbed by the different mixtures in unit time was constant.

It was found that as the partial pressure of the hydrogen was increased from zero the rate of formation of hydrogen chloride was at first almost proportional to the partial pressure of the hydrogen; but the ratio of partial pressure of hydrogen to velocity of interaction rose continuously in value as the proportion of hydrogen was increased, and when the pressure of hydrogen had attained a definite value the rate of formation of hydrogen chloride became a maximum. Then, as the proportion of hydrogen was still further increased, the rate of interaction of the chlorine and hydrogen fell very slowly. If the percentage of hydrogen is plotted against the sensitiveness, a curve of the form shown in Fig. 1 is obtained.

FIG. 1.



Results of the character just indicated were not unexpected, and, indeed, they admit of a simple explanation with the aid of the theory of photochemical change formulated in previous papers. They appear, however, to be at variance with views recently expressed by Weigert (*Ann. Physik*, 1907, [iv], **24**, 155 and 243) on the nature of photochemical changes of the class under consideration. It is desirable that the bearing of our results on these views should be briefly considered.

Weigert, from certain observations made while he was investigating the interaction of chlorine and carbon monoxide, arrived at the conclusion that the action of light is catalytic, or more precisely that the light generates nuclei, in the vicinity of which the latent or almost latent forces of affinity become abnormally active and are thus rendered capable of impelling the system into the most stable state of chemical composition. If this is a complete account of the mechanism of the photochemical interaction of chlorine and carbon monoxide, and of chlorine and hydrogen, the conclusion that the rate of the action ought to be proportional to the colourless constituent of the mixture appears to be almost inevitable. This consequence of the theory, however, is obviously not in harmony with the results of our experiments, according to which the rate of interaction of the gases is nearly independent of the proportion of hydrogen when the latter exceeds a definite value. The result on which Weigert bases his theory appears to us to be a consequence of the thermodynamic principles, and therefore consistent with any mechanical hypothesis which does not contradict those principles.*

The theory about to be advanced is of limited application, in so far as it is capable at present of being verified by quantitative relations; but it will be convenient to postpone the defining of these limitations until a general outline of the theory has been presented.

The photochemical transformation of chlorine and hydrogen into hydrogen chloride is accompanied by a fall in free energy vastly greater than the light energy required to induce the change. An hypothesis capable of giving a satisfactory mechanical account of the fact that the free energy of the system cannot, without the assistance of a relatively small supply of highly efficient external energy, break up the molecules of the elements and bring into operation the force of affinity between the atoms of chlorine and hydrogen, is not likely to be discovered until a much more intimate knowledge of the internal structure of the atoms has been gained; but it is probable, we believe, that such an hypothesis might not unprofitably be sought for in the periods of free vibration of the valency electrons. We are, however, at present only concerned with the correlation of the small but necessary supply of external energy and the extent of the chemical change induced by it.

Consider the effect of exposing to light a mixture of chlorine, hydrogen, and a relatively small amount of oxygen. The light is absorbed by the chlorine, and exists for a time in the molecules of that substance as a form of energy of vibration which is incapable without further modification of promoting the union of the hydrogen and chlorine. Of this vibrational energy by far the larger part is degraded, and thereby rendered ineffective by the agency of the oxygen, the proportion thus dissipated depending almost entirely on the partial pressures of the chlorine and oxygen, and being therefore almost the same when the concentration of both of these gases is kept constant. The vibrational energy which escapes dissipation by this process is transformed into a comparatively stable and still highly efficient form, and as such is accumulated in the chlorine molecules, which are thereby rendered abnormally active. The latter form of energy which endows the chlorine molecules with chemical activity we shall for brevity call the actinic energy. If the mixture contains no hydrogen the actinic energy is dissipated, the rate of dissipation being for the same concentration of chlorine proportional to its amount in unit volume. If the mixture contains hydrogen, however, a part only of the actinic energy will be directly dissipated, the rest being utilised and degraded in the promotion of chemical change (the proportion of actinic energy lost by direct dissipation being almost zero when the concentration of the hydrogen is high).

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* In support of his conclusions, Weigert quotes the results of Bevan (*Phil. Trans.*, 1903, *A*, **202**, 71) on cloud formation in a moist illuminated mixture of chlorine and hydrogen. For comments on Bevan's conclusion, the reader is referred to the paper on the interaction of chlorine and hydrogen by Burgess and Chapman.

We shall now show that the quantitative results are in accordance with the above view of the mechanism of the change. To this end we shall deduce from the theory what ought to occur in an element of volume of a system composed of chlorine, hydrogen, and oxygen under the influence of light. Let $U$ be the light energy absorbed in unit volume by the chlorine in unit time, and let $V$ be the vibrational energy in unit volume. The vibrational energy supplied in unit time by the light is obviously $U$, whilst that lost in unit time by dissipation is given by $CV$, $C$ being a function of the concentration of the chlorine and oxygen. In the steady state the gain and loss of $V$ must be equal, or $V=U/C$. The actinic energy acquired by the chlorine in unit time is proportional to $V$, and since $V=U/C$ it must be given by $kU$, $k$ being a function of the concentration of the oxygen and chlorine. The actinic energy in unit volume being denoted by $X$, the amount dissipated in unit time is obviously proportional to $X$, and may therefore be put equal to $cX$ ($c$ being a constant), whilst that which is degraded in bringing about the union of the chlorine and hydrogen is given by $K[H_2]X$, in which $K$ is a constant, and $[H_2]$ the concentration of the hydrogen.

Accordingly, $dX/dt=kU-cX-K[H_2]X$.

But in the steady state which is attained in an immeasurably short period of time after the commencement of the illumination $dX/dt=0$.

$$\therefore\ kU=cX+K[H_2]X.$$

The last term on the right hand side of the equation is equal to the actinic energy employed in unit time in converting chlorine and hydrogen into hydrogen chloride, and the rate of formation of hydrogen chloride may be taken as proportional to the magnitude of the same term, if we may assume—the justification for the assumption cannot be conveniently given until later—that for photochemical changes of the class to which the interaction of chlorine and hydrogen belong, the hydrogen chloride formed is proportional to the actinic energy required for its production.

When the concentration of the hydrogen is small, $kU = cX$, and therefore $X = kU/c$.

Accordingly, the rate of formation of hydrogen chloride is approximately proportional to:

$$kKU/c[\mathrm{H}_2].$$

Now $kKU/c$ is constant when the concentrations of the chlorine and oxygen, and the intensity of illumination, are kept constant—as they were in one series of our experiments—and, therefore, under such conditions the rate of formation of hydrogen chloride ought to be proportional to $[\mathrm{H}_2]$ when $[\mathrm{H}_2]$ is small.

When the concentration of the hydrogen is relatively large,

$$kU = K[\mathrm{H}_2]X,$$

the interpretation of which is that the rate of formation of hydrogen chloride ought to be approximately constant, when the light absorbed and the partial pressures of the chlorine and oxygen are kept constant as they were in a series of our experiments.

It will be seen that the experimental results are in general agreement with the requirements of the theory. It only remains to account for the gradual fall in the rate of interaction of the chlorine and hydrogen when the pressure of the hydrogen is increased from a given limiting value. We believe that this fall is due to the circumstance that hydrogen, like oxygen, is capable, although in a very limited degree, of degrading the vibrational energy from which the actinic energy is derived.*

The transformations conceived to take place in the energy associated with the chlorine molecules, and the subsequent formation of hydrogen chloride, can be conveniently summarised with the aid of the following scheme:

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* The fact that hydrogen diminishes, in a relatively slight degree, the phosphorescence of iodine vapour can be advanced in support of this view.

In the expressions developed above, the effect of the slight degradation of vibrational energy by hydrogen has been left out of account.

$$\begin{tikzcd}
 & & \mathrm{Cl_2 + low\ temperature\ heat} \\
\mathrm{Cl_2 + light} \arrow[r] & \mathrm{Cl_2 + vibration\ energy} \arrow[ru, "\text{by agency}", "\text{of oxygen}"'] \arrow[rd] & \\
 & & \mathrm{Cl_2 + actinic\ energy}\ {}^{*}\ \text{(active chlorine)} \arrow[d, "\text{with } H_2"] \\
 & & \mathrm{2HCl}
\end{tikzcd}$$

It is probable that the vibrational energy is composite, and that its character depends on the nature of the stimulating light. This question is at present under investigation.

At first sight it may not be obvious why it has been assumed that the chlorine can be associated with two distinct kinds of efficient energy designated respectively the vibrational energy and the actinic energy, the latter (to which the union of the chlorine and hydrogen is due) being derived from the former (which is degradable by oxygen, but incapable of effecting the union of the chlorine and hydrogen). The reason is that if the chlorine were associated with one kind of energy only—the vibrational energy—(which must be supposed to be both degradable by oxygen and effective in bringing about the union of chlorine and hydrogen), then clearly the rate of formation of hydrogen chloride ought continuously to approach a maximum value independent of the concentration of the oxygen as the relative proportion of impacts of chlorine molecules with oxygen and hydrogen molecules respectively is diminished, that is, as the concentration of the hydrogen is increased, that of the oxygen being constant. Whereas, of course, the maximum sensitiveness attained increases rapidly as the oxygen is diminished.

An alternative hypothesis, which is probably no more than a special case of the foregoing, is the following. The fraction of the vibrational energy which is not dissipated by the agency of the oxygen converts some of the chlorine into a very unstable and active allotropic modification, which is capable of reacting with hydrogen. If a sufficient number of hydrogen molecules are present in unit volume of the mixture practically every active chlorine molecule generated by the influence of the light makes a fruitful impact with a hydrogen molecule, and since the number of active chlorine molecules produced is proportional to the light absorbed, the hydrogen chloride formed under these conditions will also be proportional to the light absorbed. If, however, the hydrogen molecules are scarce, most of the active chlorine molecules will, on account of their extreme instability, revert to inactive molecules, and only a small number of them will make fruitful impacts, the percentage of active molecules which make fruitful impacts being proportional to the concentration of hydrogen.

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* It is possible that Strutt's active form of nitrogen consists of ordinary molecules of nitrogen rendered active in the same way as we conceive that chlorine molecules are rendered by the agency of light.

It is now desirable that we should examine a little more closely the energetics of the hydrogen–chlorine reaction. We shall, thereby, be enabled to offer further justification for our main assumption, namely, that the quantity of actinic energy and the amount of chemical change induced by it are equivalent, or, in other words, that the decrease in $X$ attributable solely to the formation of hydrogen chloride is proportional to the hydrogen chloride produced. We shall be enabled also to define the class of chemical change to which the same assumption may be legitimately applied.

It is a simple matter to show that the fall in free energy during the formation of two gram-molecules of hydrogen chloride is given by the expression:

$$Rt\left(\log_e \frac{[\mathrm{HCl}]'^2}{[\mathrm{H_2}]'\,[\mathrm{Cl_2}]'} - \log_e \frac{[\mathrm{HCl}]^2}{[\mathrm{H_2}]\,[\mathrm{Cl_2}]}\right),$$

in which a symbol enclosed in square brackets signifies the concentration of the gas corresponding with the symbol, and a square bracket with a dash indicates a concentration in a system in equilibrium.

If $[\mathrm{HCl}]'$ is made equal to $[\mathrm{HCl}]$, the expression reduces to:

$$Rt \log_e \frac{[\mathrm{H_2}]\,[\mathrm{Cl_2}]}{[\mathrm{H_2}]'\,[\mathrm{Cl_2}]'}.$$

Now in ordinary circumstances the product $[\mathrm{H_2}]'[\mathrm{Cl_2}]'$ is extremely small in comparison with $[\mathrm{H_2}]\,[\mathrm{Cl_2}]$, and therefore the numerical value of the above expression is large, and will be very little affected by very appreciable alterations in either $[\mathrm{H_2}]$ or $[\mathrm{Cl_2}]$.

Accordingly, the efficient energy in the system itself available for the purpose of converting the chlorine and hydrogen into hydrogen chloride is almost constant, that is, is almost independent of the pressure of the hydrogen or chlorine. In other words, the tendency of the chlorine and hydrogen to change into hydrogen chloride is almost independent of the partial pressure of the former gases; and, therefore, if in addition to the energy of the system a small quantity of energy of greater efficiency than that contained in the system is required to bring about a definite amount of chemical change, the quantity of additional energy will be constant, it being assumed, of course, that its quality is the same. Our principal assumption could not be made for a system near the condition of equilibrium, since in that case a small variation in the concentration of one of the interacting constituents would appreciably alter the tendency of the change to take place in a given direction, and therefore the additional supply of actinic energy required to bring about a stated amount of chemical change would not be independent of the constitution of the system.

It will consequently be perceived that without modification the above theory can only apply to photochemical changes of the same class as that under consideration, namely, to those changes which are attended by a considerable fall of chemical potential. It is, we believe, impossible to elaborate a satisfactory quantitative theory of the dynamics of photochemistry applicable to every class of chemical change without the assistance of much more experimental information than is at present available for the purpose.

## EXPERIMENTAL.

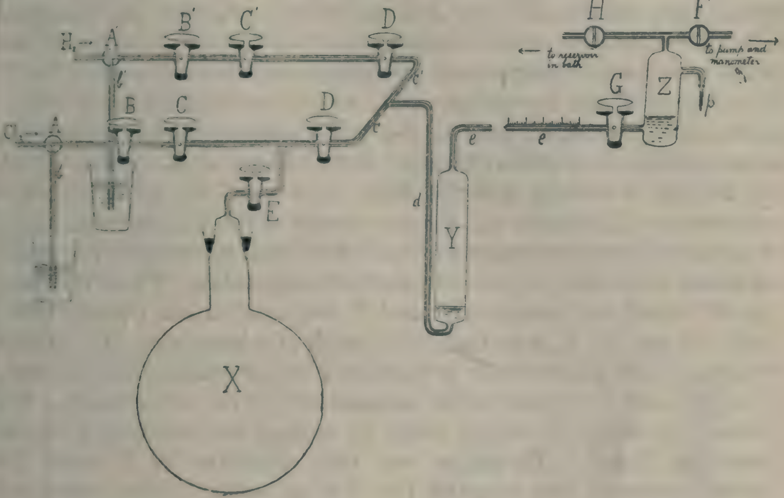
The chlorine and hydrogen were prepared by the electrolysis of concentrated hydrochloric acid. In the preparation of the hydrochloric acid the greatest care was taken to prevent contamination with organic impurities, as these would have furnished inhibitors which could only have been removed from the interacting gases with extreme difficulty, and trustworthy actinometric measurements cannot, of course, be made so long as the chlorine and hydrogen contain the least trace of inhibitive impurity. Into chlorine-water which had been boiled for many hours hydrogen chloride was passed until the liquid was saturated. The hydrogen chloride was prepared by the action of concentrated sulphuric acid on common salt. The common salt was prepared in the usual way by its precipitation from a solution of brine with hydrogen chloride. In order to destroy organic impurities in the concentrated sulphuric acid, the latter was first heated with chlorine, and then, after sodium peroxide has been dissolved in it, boiled until the resulting persulphuric acid had been destroyed. The apparatus employed to electrolyse the hydrochloric acid has already been described (Chapman and MacMahon, T., 1909, **95**, 135).

A diagrammatic representation of the essential part of the apparatus is given in Fig. 2.

*X* is a large globe which is used to contain the mixture of chlorine and oxygen. *Y* is the insolation vessel of the actinometer which is immersed in a large glass tank filled with water, the water being kept at a constant temperature of 20° with the aid of an electric thermo-regulator. The index tube *e* of the actinometer communicates through the tap *G* with the reservoir *Z*. By opening the tap *F* the reservoir can be brought into communication with a water-pump and a manometer, neither of which are shown in the diagram. The reservoir is also in connexion with a large glass bottle immersed in the same tank as the actinometer, the pressure above the liquid in $Z$ being thereby maintained constant.

The filling of the globe $X$ was accomplished in the following way: The hydrochloric acid was electrolysed, and the chlorine and hydrogen permitted to escape through the tubes $b$ and $b'$ until all the air had been expelled from the cell and delivery tubes. In the meanwhile, before water had been introduced into $Y$ and $Z$, the apparatus, including the globe, from the taps $B$, $B'$, and $H$ to the pump was exhausted. After closing $H$, the tap $B$ was very cautiously turned just sufficiently to admit chlorine to the exhausted apparatus at such a rate that the gas did not cease to enter slowly the potassium hydroxide solution under $b$. When the pressure in the globe had risen to about 15 cm. of mercury, the apparatus was again exhausted. The operation of filling with chlorine to 15 cm. and exhausting was repeated four times. The taps $D$ and $D'$ were then closed, and the globe $X$ completely filled with chlorine, an operation which took about six hours. The pressure in the globe was then reduced below the atmospheric pressure to an extent depending on the amount of oxygen it was desired to introduce into the globe. After the tap $E$ had been closed, the potassium hydroxide solution removed from under $b$, the electrolysis of the hydrochloric acid in the cell discontinued, and the three-way tap $A$ turned so that $b$ communicated with the apparatus and not with

FIG. 2.



the cell, a slow stream of oxygen was passed through *b* in the direction *A*, *B*, *C*, *D*, etc., until the chlorine had been removed from the capillary tubes. The tap *E* was next opened, and the oxygen permitted to enter the globe until the pressure was again that of an atmosphere. Then the tap *E* was closed, and the oxygen and chlorine in the globe allowed to mix, a process for the completion of which it was found desirable to assign at least two days. Water which had been previously digested for many hours with chlorine was introduced into the reservoir *Z* through the side-tube *p*, which was drawn out to a capillary tube to permit of its being easily opened and closed by respectively breaking off the tip with the aid of a file, and fusing up the open end before the blow-pipe. Of the water thus introduced into *Z* a convenient quantity was admitted into the insolation vessel through the tap *G*, the pressure in the insolation vessel having been previously reduced below that in *Z*. The filling of the insolation vessel with a mixture of known composition of hydrogen and of the gas contained in the globe was accomplished in a similar manner to the filling of the globe. With *B*, *B′*, and *E* closed, and the other taps open, the apparatus was exhausted. Hydrogen was then admitted to the apparatus through *B′*, and pumped out again several times until all oxygen had been removed from the actinometer and delivery tubes. Then with the tap *D′* closed the insolation vessel *Y* was washed out several times with the gas in *X*, and then filled with the same gas. By gently shaking *Y* the water which it contained was saturated with chlorine. The pressure in *Y* was then reduced to 30 cm. of mercury, the precaution being, of course, taken to remove the excess of chlorine from the liquid. Hydrogen was then admitted to *Y* until its partial pressure had reached the desired value. This operation demanded the exercise of some care; it was accomplished by adjusting the pressure in *Z* to the required value, allowance being made for the liquid contained in the vessel, then admitting hydrogen into the insolation vessel very slowly with the tap *G* partly turned on, so that the liquid in the index *e* could only move slowly in the direction of lower pressure, and when the forward movement of the index liquid had ceased, turning the tap *G* full on, the hydrogen being shut off as soon as the index liquid had reached the zero point on the scale.

The insolation vessel of the actinometer was illuminated with a Hefner lamp. The position of the lamp was unaltered during a series of observations; but in order to secure a convenient rate of formation of hydrogen chloride the intensity of illumination was altered from series to series, being greater for mixtures which contained a larger amount of oxygen. When the mixture is exposed to light great care must be taken that the index has come to its position of equilibrium before taking the initial and final readings of its position. Attention to this precaution is particularly necessary after the mixture has been exposed to light, as the index recedes slowly for several hours after hydrogen chloride has been formed in the insolation vessel. This apparent expansion of the gas in the actinometer after exposure to light has been found to be due to the formation of a supersaturated solution of chlorine in the liquid enclosed in the insolation vessel, and to this solution slowly giving up its excess of chlorine. The excess of chlorine passes out of solution more rapidly, of course, if the actinometer is gently shaken. The cause of the formation of a supersaturated solution of chlorine is fairly obvious. The hydrogen chloride generated by the action of the light dissolves in the surface layer of water, and in the concentrated hydrochloric acid produced the chlorine is extremely soluble. The solution of chlorine in concentrated hydrochloric acid is, however, rapidly diluted by the process of diffusion, and the chlorine being less soluble in dilute hydrochloric acid tends to escape. The relative amount of hydrochloric acid produced in unit time is obtained by dividing the product of the total movement of the index and the pressure of the gas in the actinometer by the time of exposure. The results are tabulated below:

| Series. | $\frac{\text{Pressure of hydrogen}}{\text{Pressure of chlorine}}$. | Pressure of oxygen in cm. of mercury. | Sensitiveness. |
|---|---|---|---|
| I. | 0·485 | very small | 1000 |
| | 0·894 | ,, ,, | 786 |
| II. | 0·511 | 0·25 | 1000 |
| | 1·000 | 0·25 | 682 |
| | 1·472 | 0·25 | 636 |
| | 0·0235 | 0·25 | 489 |
| III. | 0·510 | 0·60 | 1000 |
| | 1·020 | 0·60 | 734 |
| | 1·469 | 0·60 | 689 |
| | 0·0318 | 0·60 | 431 |
| IV. | 0·510 | 0·60 | 1000 |
| | 1·536 | 0·60 | 688 |
| V. | 0·521 | 1·20 | 1000 |
| | 1·579 | 1·20 | 837 |

It will be observed from the above table that a mixture which contains equal volumes of chlorine and hydrogen is not twice as sensitive as one which contains only 3 per cent. of the latter gas.

The pressure of the chlorine was nearly 30 cm. in all the experiments. For the purpose of comparison the sensitiveness of each mixture is compared with that of the mixture in the same series which contained two volumes of chlorine to one of hydrogen. The numbers given for the sensitiveness are the means of several determinations in most cases.

The fall in sensitiveness resulting from an increase in the proportion of hydrogen present appears to be less marked as the pressure of oxygen is increased.

It will be observed that a mixture which contains equal volumes of chlorine and hydrogen is never the most sensitive, the maximum sensitiveness being given by a mixture containing a considerably lower proportion of hydrogen.

Sir Leoline Jenkins Laboratory,
Jesus College, Oxford.

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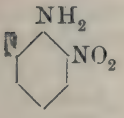
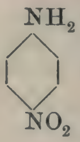
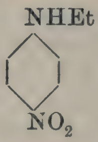
# LVI.—*Quinonoid Salts of Nitroanilines.*

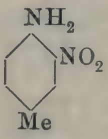
By Arthur George Green and Frederick Maurice Rowe.

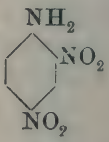
In a previous communication (T., 1912, **101**, 2452) indirect evidence has been adduced in favour of the view that in alkaline solutions the orthonitroamines of the benzene series exist (in part at least) in the form of salts of the quinonoid type, $\mathrm{R}\ll^{\mathrm{NH}}_{\mathrm{NO_2M'}}$. With the object of isolating such salts in an analysable form and of investigating their conditions of formation, we have examined the behaviour of a number of nitroamines, ortho, meta, and para, on treatment in benzene solution with sodium ethoxide. The following nitroamines gave under these conditions deep orange to red precipitates of the sodium salts insoluble in benzene:

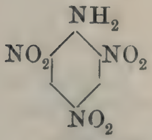


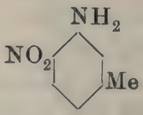


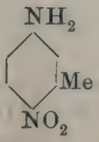


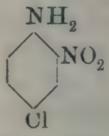


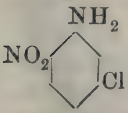


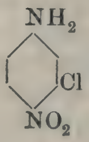


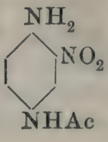


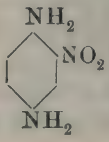




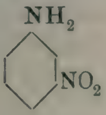


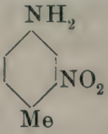


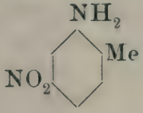


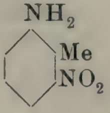


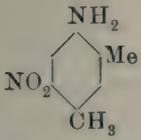
On the other hand, no precipitates were obtained, and no change of colour was observed with the following:

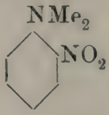


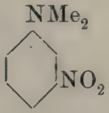


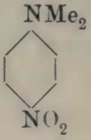








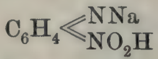




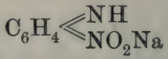
It would therefore appear that all primary and secondary ortho- and para-nitroamines give rise to deeply-coloured salts under the conditions employed, but that no such quinonoid change occurs in the meta-series. It is also apparent from the behaviour of the *o*- and *p*-nitrodimethylanilines that no salts are obtainable when both hydrogen atoms of the amino-group are replaced by alkyl groups. The absence of reaction in the meta-series is noteworthy in view of the still open question of the existence of meta-quinonoid compounds (compare Hantzsch, *Ber.*, 1906, **39**, 1096; Meyer and Desamari, *Ber.*, 1908, **41**, 2437; Stark and Garben, *Ber.*, 1913, **46**, 659).

The quinonoid salts of the ortho- and para-nitroamines are very unstable substances, becoming rapidly decolorised on exposure to damp air. In order to obtain the compounds in an analysable form it is necessary to work rapidly, and to carefully exclude all moisture by the use of solvents dried over sodium. The precipitates were collected quickly on a Büchner funnel, washed with hot dry benzene, followed by anhydrous ether, and finally dried in a vacuum desiccator over sulphuric acid. They form deep yellow, orange, or red powders insoluble in benzene. In the dry state they can be kept unchanged, but on treatment with water they are hydrolysed at once, giving the parent nitroamine, and leaving free alkali hydroxide in solution. On this fact was based a method for their analysis. A weighed quantity of the dry salt was treated with water, and the precipitated nitroamine separated and washed free from alkali. The filtrate and washings were then titrated with standard sulphuric acid, employing methyl-orange as indicator. In every case the results correspond closely with those required for a monosodium or monopotassium salt of the quinonoid nitronic acid, $R{\lessgtr}^{NH}_{NO_2H}$. The possibility of these salts having a quinolnitronic acid constitution, $\begin{matrix}EtO\\NH_2\end{matrix}{>}R{:}NO_2M'$, analogous to that which has been assigned to the coloured salts derived from *s*-trinitrobenzene and from picrylaniline (compare Busch and Kögel, *Ber.*, 1910, **43**, 1549), is excluded by the absence of ethyl groups (negative result with Zeisel test). It was further ascertained by blank experiments that under the conditions employed no concomitant precipitation of sodium ethoxide can occur.

In the case of *p*-nitroaniline two differently coloured sodium salts were obtained, a yellow and a red, according to the conditions employed. The red salt is fairly stable in the presence of an excess of *p*-nitroaniline, but as soon as a quantity of sodium ethoxide is added sufficient to produce alkalinity of the benzene solution (dry phenolphthalein paper as indicator) it changes suddenly into the yellow and more stable form. When *p*-nitroaniline is replaced by its monoethyl derivative only one salt was obtainable, and this appeared to correspond with the yellow form. This observation seems to lend some support to the possibility that the two salts of *p*-nitroaniline may be constitutionally isomeric in the sense of the formulæ:

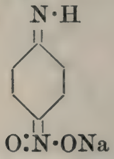

$C_6H_4<^{NNa}_{NO_2H}$

and

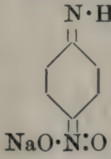

$C_6H_4<^{NH}_{NO_2Na}$

Red salt (labile). Yellow salt (stable).

On the other hand, in view of the fact that we failed to obtain a disodium salt of *p*-nitroaniline, $C_6H_4<^{NNa}_{NO_2Na}$, by employing a large excess of sodium ethoxide, and that similar pairs of coloured isomerides have been met with by Hantzsch in the case of the nitrophenol salts and by Sudborough and Picton (T., 1906, **89**, 586) in the case of free picrylarylamines (see also Hantzsch, *Ber.*, 1910, **43**, 1651, 1662), it appears more probable that the isomerism is of the kind termed by Hantzsch "chromoisomerism," and is possibly produced by differences in sterical configuration; thus the two salts in question might be represented by the formulæ:

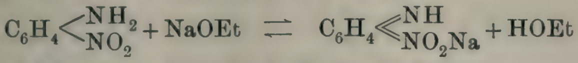


and



Red salt (labile). Yellow salt (stable).

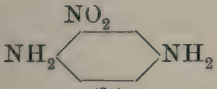
It may be noted that under the conditions in which all the quinonoid salts were prepared (benzene or toluene containing a little alcohol) these salts undergo a certain degree of dissociation. This is least at the boiling point of the solvent, but increases rapidly as the temperature is lowered, until in a freezing mixture the precipitate (in the case of *o*- and *p*-nitroaniline) disappears completely, leaving a pale yellow solution of the free nitroaniline. On heating this cooled solution the precipitation of the coloured sodium salt recommences, and is again almost complete at the boiling point. The equilibrium of the system:



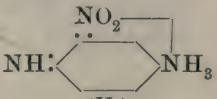
$$C_6H_4{<}\begin{matrix}NH_2\\NO_2\end{matrix} + NaOEt \rightleftharpoons C_6H_4{\ll}\begin{matrix}NH\\NO_2Na\end{matrix} + HOEt$$

is therefore determined to the right by high temperatures, to the left by low.

The tendency of nitroamines to give quinonoid salts is further exemplified by the behaviour of nitro-*p*-phenylenediamine. This compound crystallises from water in magenta-red needles, having a dark green reflex. In water and in alcohol it dissolves (0·1 per cent. solutions) with a deep blood-red colour, and from the aqueous solution wool is dyed nearly the same shade. On the other hand, the solutions of the substance in benzene, toluene, or xylene (0·1 per cent. solutions) are yellow, those in chloroform and ether a rather redder yellow, and those in acetone and nitrobenzene an orange tint intermediate between the colour of the alcoholic and benzene solutions. The monohydrochloride of the base is bright yellow. These facts point to the conclusion that whilst the ordinary formula (I) correctly represents the constitution of the base in hydrocarbon solvents, the solid substance is actually an internal quinonoid salt of the formula (II), which in the main is also the condition of the compound in its aqueous and alcoholic solutions and when dyed on animal fibres. In solvents of intermediate ionising power a mixture of the two forms is present. The addition of sodium ethoxide to the yellow benzene solution causes the precipitation of a dark red sodium salt of very similar colour to that of the free compound in the solid state.



(I.)



(II.)

## EXPERIMENTAL.

### *Sodium Salt of o-Nitroaniline.*

It was found advisable in this case to employ the nitroamine in excess. Twenty-five c.c. of a benzene solution of sodium ethoxide, obtained by dissolving 1 gram of sodium in 15 c.c. of absolute alcohol, and diluting with dry benzene to 100 c.c., were added to a boiling solution of 2 grams of *o*-nitroaniline in 120 c.c. of dry toluene. The brownish-red precipitate was collected while hot, washed, and dried as already described. It forms a reddish-brown powder, which on contact with water yields *o*-nitroaniline. Titration with sulphuric acid gave Na = 14·31 (mean). $C_6H_5O_2N_2Na$ requires Na = 14·37 per cent.

### *Sodium Salt of* p-*Nitroaniline* (*Red Form*).

Fifty c.c. of a benzene solution of sodium ethoxide, obtained as above, were added quickly to a hot solution of 6 grams of *p*-nitroaniline in 450 c.c. of dry toluene. The orange-red precipitate was collected at once, and boiled with 150 c.c. of dry toluene to remove excess of *p*-nitroaniline. The precipitate was again collected, and washed with boiling toluene, followed by anhydrous ether. The dry salt is orange-red. Titration with sulphuric acid gave Na = 14·28 (mean). $C_6H_5O_2N_2Na$ requires Na = 14·37 per cent.

### *Sodium Salt of* p-*Nitroaniline* (*Yellow Form*).

Thirty c.c. of the same benzene solution of sodium ethoxide were added to a boiling solution of 2 grams of *p*-nitroaniline in 150 c.c. of dry benzene. The yellow precipitate was collected and washed with benzene and ether. By treatment with water *p*-nitroaniline is regenerated.

Found: Na = 14·22 (mean).

$C_6H_5O_2N_2Na$ requires Na = 14·37 per cent.

### *Sodium Salt of* p-*Nitroethylaniline.*

Thirteen c.c. of a solution of sodium ethoxide obtained by dissolving 1 gram of sodium in 15 c.c. of absolute alcohol and diluting with dry benzene to 50 c.c. (that is, double the strength of that used before) were added to a solution of 2 grams of *p*-nitroethylaniline in 50 c.c. of dry toluene. The precipitate, although orange-yellow at first, rapidly darkens in colour, and appears to undergo a certain amount of decomposition.

Found: Na = 12·28 (mean).

$C_8H_9O_2N_2Na$ requires Na = 12·23 per cent.

### *Sodium Salt of* m-*Nitro*-p-*toluidine*, ($CH_3 : NH_2 : NO_2 = 1 : 4 : 3$).

This was prepared in the same manner as the sodium salt of *o*-nitroaniline. It forms a reddish-brown powder of redder shade than the *o*-nitroaniline salt.

Found: Na = 13·28.

$C_7H_7O_2N_2Na$ requires Na = 13·22 per cent.

### *Potassium Salt of* 2:4-*Dinitroaniline.*

Twenty c.c. of a solution of alcoholic potassium hydroxide obtained by dissolving 1 gram of potassium hydroxide in 30 c.c. of absolute alcohol were added to 2 grams of dinitroaniline dissolved in 250 c.c. of dry benzene. The purplish-crimson precipitate which separated was collected, washed, and dried as before. The dry salt forms a purplish powder. It readily deflagrates on heating. On treatment with water dinitroaniline was regenerated.

Found: K=17·33 (mean).

$C_6H_4O_4N_3K$ requires K=17·65 per cent.

The sodium salt, prepared by employing sodium ethoxide, is similar in appearance and properties.

### *Potassium Salt of* 2:4:6-*Trinitroaniline* (*Picramide*).

This was prepared in the same manner as the preceding. The dry salt has a reddish-brown colour, and explodes violently on heating to about 110°.

Found: K=14·53 (mean).

$C_6H_3O_6N_4K$ requires K=14·66 per cent.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
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## LVII.—*The Estimation of Mercury as Metal by the Dry Method.*

By ALEXANDER CHARLES CUMMING and JOHN MACLEOD.

MERCURY compounds, when heated with calcium oxide, are decomposed according to the equation:

$$2HgX + 2CaO = 2CaX + 2Hg + O_2.$$

Nearly seventy years ago Erdmann and Marchand (*J. pr. Chem.*, 1844, **31**, 385) applied this reaction to the determination of the atomic weight of mercury. Their method has since been used for the estimation of mercury (König, *J. pr. Chem.*, 1857, **70**, 64). Treadwell ("Analytical Chemistry," English edition, 1908, **2**, 136) recommends this method as giving exact results, but states that it is nevertheless preferable, when possible, to precipitate as sulphide.

Many modifications have been proposed at different times, and there is general agreement that results of a high degree of accuracy are attainable, but that the method is troublesome. The original method could not be used for mercuric iodide, but Rose (*Ann. Phys.*

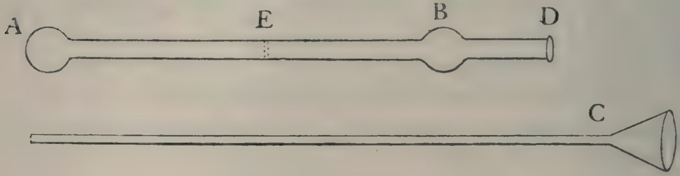
*Chem.*, 1860, [ii], **110**, 542) found that accurate results were obtained if finely divided copper was added to the mixture of mercury salt and lime.

The special advantage of the dry method is that it is applicable to ores and minerals without previous removal of any other metals. The disadvantage is, as we have already indicated, the experimental difficulty; we believe that this has been largely overcome by the use of the apparatus and by the procedure described below.

## EXPERIMENTAL.

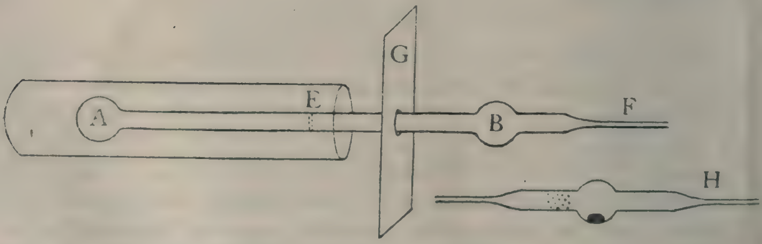
The apparatus used by Penfield (*Amer. J. Sci.*, 1894, [iii], **48**, 31) for the determination of water in minerals was found suitable for our purpose. A piece of glass tubing about 20 cm. in length and 5 mm. in diameter was closed at one end, and small bulbs blown at *A* and *B* (Fig. 1).

FIG. 1.



The tube was cleaned, dried, and weighed. By means of the long funnel, *C*, a suitable quantity of the substance to be analysed was introduced into the bulb *A*, and the tube and contents weighed.

FIG. 2.



A mixture of iron filings and quicklime was then added by means of the funnel *C*, from which any adhering traces of the substance had meanwhile been removed. The mixture introduced into the bulb *A* consisted mainly of iron filings, which were well mixed with the substance by rotating the tube. A mixture of about equal parts of iron filings and quicklime was then added until about 8 cm. of the tube had been filled. A small plug of asbestos, *E*, was introduced, so that, after tapping the tube, only a very shallow air-channel remained along the top. The open end, *D*, was then drawn out into a fine capillary, as in *F*, Fig. 2.

The prepared tube was placed in an iron tube which could be heated by a flat-flamed burner. (We used a piece of iron gas-pipe about 15 cm. by 1·5 cm., and closed the ends with plugs of asbestos fibre.) The bulb *A* was wrapped in some asbestos paper to prevent it coming into direct contact with the iron tube, and thereby being heated before the narrow part of the tube; if this precaution was omitted, the mercuric salt was partly volatilised without decomposition.

An asbestos shield, *G*, prevented the heat from reaching the bulb *B*, which was cooled by wet filter paper.

The iron tube was heated, at first with a small flame and at the end nearer *G* only. The heating was gradually increased, and the flame moved backwards until the whole iron tube was heated to a low red heat. The apparatus was almost horizontal, but the end *F* was slightly lower than the closed end, so that, on gently tapping the tube, any mercury which had condensed beyond the asbestos screen formed a globule and ran into the bulb *B*. When all the mercury had distilled (usually after one hour) the glass tube was drawn out until the plug *E* was exposed. At the same time the burner was drawn forward, so that the flame played directly on the glass tube. As soon as the glass tube became red hot it was drawn off about midway between the plug *E* and the bulb *B*. The mercury was thus obtained in a tube, as shown at *H* in Fig. 2.

It was observed that if the remainder of the original tube was left with only a small portion projecting from the hot furnace, any residual mercury collected in the exposed cooler portion of the tube. By examination with a lens very small quantities of mercury could be detected in this way, and a useful check on the analysis was thereby obtained.

To remove water, a current of dry air was drawn through the tube until the weight was constant. The main portion of the mercury was then shaken out of the tube, and the portion adhering to the glass removed by blowing air through the gently heated tube. The empty tube was cooled and weighed.

*Mercury in Mercuric Chloride.*—The percentage of mercury in a commercial pure specimen of mercuric chloride was determined by the above method:

(1) 0·8097 gave 0·5957 Hg. Found: Hg = 73·57. Calc., Hg = 73·88 per cent.

(2) 0·9950 gave 0·7358 Hg. Found: Hg = 73·94. Calc., Hg = 73·88 per cent.

*Mercury in Mercuric Sulphide.*—On trying this method with the sulphide it was not found possible to retain all the sulphur by the mixture of iron and quicklime. It was found that accurate results were obtained when lead chromate was also added. A mixture of one part of quicklime, two parts of iron filings, and one part of powdered lead chromate gave satisfactory results with both mercuric sulphide and iodide. The following results were obtained:

(1) A pure specimen of mercuric sulphide was prepared by precipitation, and free sulphur removed by extraction with boiling carbon disulphide:

0·6352 gave 0·5447 Hg.
Found: Hg = 85·75. Calc., Hg = 86·22 per cent.

(2) With a specimen of black mercuric sulphide:

0·6278 gave 0·5385 Hg.
Found: Hg = 85·78. Calc., Hg = 86·22 per cent.

*Mercury in Cinnabar.*—The amount of mercury in a sample of cinnabar was found by the sulphide method to be 59·06 per cent.:

0·8303 gave 0·4880 Hg. Found: Hg = 58·77 per cent.

*Mercury in Mercuric Iodide.*—The following results were obtained with a pure dry specimen:

(1) 0·5878 gave 0·2593 Hg.
(2) 0·7704 „ 0·3398 Hg.
Found: Hg = 44·11. Calc., Hg = 44·14 per cent.

These results show that the method is accurate, and we have found it convenient and easy in practice. For the estimation of mercury in a mixture of unknown composition, 0·5 to 1·0 gram should be heated in the manner described with 2·5 to 3·0 grams of the iron, quicklime, and lead chromate mixture.

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# LVIII.—*The Latent Heats of Chloroform and Benzene and of their Mixtures Between* 0° *and* 80°.

By JAMES FLETCHER and DANIEL TYRER.

A FAIRLY comprehensive investigation of the latent heats of binary mixtures of liquids has already been completed by one of the authors (T., 1911, **99**, 1633; 1912, **101**, 81, 1104), but the determinations were all made at the boiling points of the mixtures, and all the results obtained refer to these somewhat arbitrary temperatures. In this investigation the latent heats of various mixtures of two normal liquids, namely, chloroform and benzene, have been made at temperatures varying from 0° to about 80°, and the results furnish data for a complete study of the laws governing the latent heats of mixtures. It has been pointed out (T., 1911, **99**, 1633) that a mixture can be regarded as having two latent heats termed "latent heat at constant external pressure" and "latent heat at constant composition."

For a definition and explanation of these terms the reader is referred to the above-quoted papers. It may be mentioned that in the previous work only latent heats at constant pressure were experimentally determined, latent heats at constant composition being calculated from these results for a series of arbitrary temperatures. In the present paper a method is described for determining experimentally latent heats at constant composition at any temperature below the boiling point, and results are set forth for various mixtures of chloroform and benzene, two typically normal liquids.

If 1 gram of a mixture be placed in a vessel immersed in a thermostat and the pressure on the vessel be maintained equal to or slightly less than the saturation vapour pressure of the mixture, the liquid will completely evaporate, and in so doing absorb a certain amount of latent heat from the thermostat. This absorbed latent heat is precisely what we have measured. Of course, it will be clear that in the vaporisation the pressure does not remain constant, but gradually falls until the liquid is all evaporated, and a certain amount of external work is done against this pressure, and this external work is included in the absorbed latent heat. The results obtained for a given mixture at various temperatures should be comparable to the latent heats of a pure liquid at the same temperatures and evaporated under its own vapour pressure.

### *The Method and Apparatus.*

The method adopted was similar in principle to that used by Griffiths and Marshall in their determinations of the latent heats of benzene (*Phil. Mag.*, 1896, [v], **41**, 1). As, however, our method differs from theirs in many respects it may be described here in full.

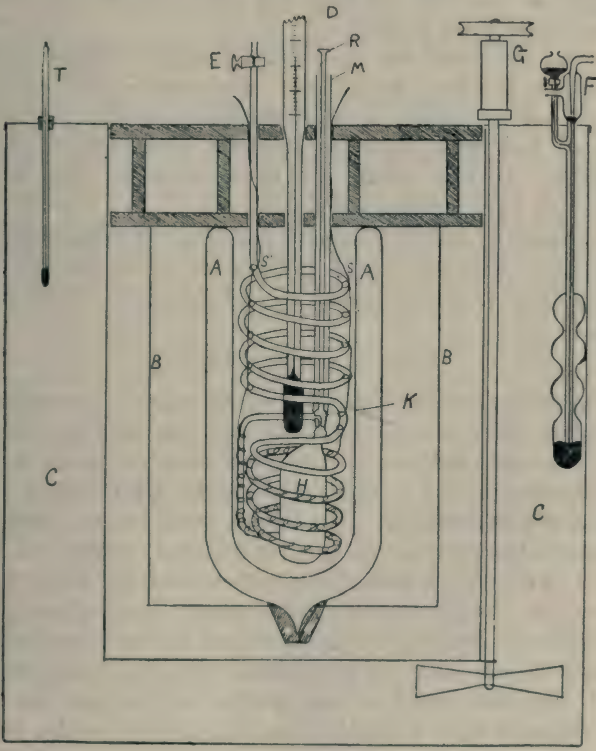
When 1 gram of chloroform is evaporated in a calorimeter containing 300 grams of water only about 60 calories are absorbed, causing a temperature change of only 0·2°. The measurement of so small a change with even a moderate degree of accuracy is quite impossible even on the finest graduated mercury thermometers. It is clear, therefore, that the ordinary method of direct measurement of the temperature change cannot be used. Instead of measuring the temperature change with a thermometer, we measure it indirectly by heating electrically the calorimeter by just so much as it was cooled in the vaporisation of the chloroform and measuring the current used in the heating. The current is measured by means of a silver voltameter, and we are enabled in this manner to interpret the temperature change due to the vaporisation of the chloroform in terms of the weight of silver deposited in the voltameter. It was found that a temperature change of 1° corresponds roughly with the deposition of about 0·3 gram of silver, and as this can be weighed accurately to less than 0·0001 gram it is thus possible to measure in this indirect manner temperature changes accurately to less than 0·0003°, supposing, of course, that the temperature after the experiment is just the same as before. In addition to this advantage we are by this method independent of:

(1) Accuracy of the thermometer,

(2) An exact knowledge of the specific heat of the calorimeter and contained liquid.

Further, by surrounding the calorimeter with a large bath maintained at a temperature the same or a little above that of the calorimeter, we can eliminate cooling corrections altogether or make them very small.

The calorimeter can best be explained by reference to the figure. The calorimeter proper consists of a large Dewar vessel, *A*, of about 400 c.c. capacity. This is contained in a cylindrical vessel, *B*, made of tinned sheet iron. This in turn is contained in a large double-walled copper tank, *C*, containing about 30 litres of water, and provided with a thermometer, *T*, a thermo-regulator, *F*, and a rotatory stirrer, *G*, which is actuated by a small electric motor. This outer bath of water is heated from below with burners, and maintained at such a temperature that the liquid in the Dewar vessel remains at a constant temperature, as indicated by the Beckmann thermometer, *D*. The liquid the latent heat of which is to be measured is contained in the vessel *H*, which is provided with a tap, *K*, which by turning the tap-rod *R* can be opened or closed to the glass spiral tube On the coils of this spiral tube is wrapped about 100 cm. of 0·02 cm. platinum wire fused on at *S* and *S′* to two pieces of copper wire of negligible resistance, and which are brought outside the calorimeter as shown. The spiral tube also serves as a stirring rod by arranging it so that it can be raised up and down by means of a small motor and crank. The calorimeter is provided with a lid, as shown, which at first was made of wood, but later was made of hard asbestos board.



The Beckmann thermometer used in these experiments was one selected from six others, and was easily readable to 0·001°. To prevent sticking of the mercury thread it was constantly tapped during an experiment by a small electrical hammer. The absolute value of the readings was found by preliminary comparisons with a standard thermometer.

### *The Electrical Apparatus.*

The general arrangement of the electrical portion may be described as follows. A storage battery of about five cells was connected with the heating coil in the calorimeter, with the voltmeter, and silver voltameter. The voltameter and voltmeter could be thrown out of circuit by switches, and thus allow a preliminary current to pass through the coil. This was used simply to adjust the temperature to the desired point. All the electrical contacts were soldered wherever possible, and the switches were of a heavy type, and made good contact.

The voltmeter used was a Weston standard voltmeter readable with accuracy to about 0·005 volt. The error in the voltage reading would not be greater on the average than 0·05 per cent. This instrument had been used in previous work, and always found trustworthy. It was tested before commencing this work, and found not to have altered during its use.

The voltameter was the usual form of silver voltameter, a plate of pure silver dipping into a solution of silver nitrate, which is contained in a platinum basin of suitable size, which forms the cathode.

### *Working of the Apparatus.*

The liquid in the calorimeter may be either pure water or any other liquid of known specific heat and low vapour pressure. In the present work a series of determinations was made with water in the calorimeter, and then the whole series was repeated with pure aniline in the calorimeter. The Dewar vessel is first filled within a few centimetres of the top with a weighed amount of water or aniline. The spiral is placed in position, and the lid of the calorimeter put on. The Beckmann thermometer, having been previously adjusted to the desired temperature and the absolute value of its zero point determined by comparison with the standard, is now inserted into the liquid of the calorimeter so that its bulb lies within the coils of the spiral tube. The liquid in the calorimeter is heated by means of a shunted current to the desired point, and the liquid the latent heat of which is to be measured is introduced into the bulb of the spiral tube. This is done by aid of a closed dropping funnel which is provided with a long narrow delivery tube, which can be inserted into the bulb of the evaporating spiral. At the end of the delivery tube is provided an inner nozzle and a ground cap to prevent the loss of the adhering drop of liquid. The delivery vessel is filled with the liquid, and weighed by suspending it on the balance. The ground glass cap is then removed and also the rod *R* of the tap (see figure), the long tube of the delivery funnel is inserted into the spiral, and an amount of the liquid run into the bulb *H*. The delivery vessel is then withdrawn, the ground glass cap and rod *R* replaced, and the delivery vessel weighed again. This gives the weight of liquid introduced.

The taps *K* and *E* of the spiral tube are closed. The motors which actuate the stirring of the liquid in the calorimeter and also in the water tank are now switched on, and observations of the Beckmann thermometer are made every two minutes. If the calorimeter is cooling, the temperature of the outer bath is raised, and vice versa. When the temperature of the calorimeter is constant or changes only very slowly, the rate of cooling per minute is carefully measured.

This enables one to make a small correction for the natural cooling or heating of the calorimeter during the course of the experiment. The end of the tube *E* is now attached by thick-walled rubber tubing to a strong water-pump and with a wash-bottle containing sulphuric acid to serve as an indicator of the rate of evaporation. The tap *K* is opened full and the tap *E* slightly, so that if it were opened wider the bubbling in the wash-bottle would proceed faster. This ensures that the vaporisation proceeds under the true vapour pressure of the particular liquid under investigation. The temperature as indicated by the Beckmann thermometer now slowly falls. After it has fallen a few tenths of a degree the current is switched on, and the temperature rises again. It is allowed to rise to a few tenths of a degree above the original temperature, and then the current is turned off. The temperature now falls below the original point, and by this time all the liquid has evaporated, which is indicated by the cessation of the bubbling in the wash-bottle. The current is now turned on again, and the mercury thread of the thermometer allowed to rise until on switching off the current it is brought back to the original point. Usually the initial and final temperatures are not absolutely identical, but differ by anything between 0° and 0·03°. The difference is carefully read off on the Beckmann thermometer, and a small correction made for it. This correction depends on (*a*) the assumed accuracy of the thermometric reading, (*b*) a knowledge of the specific heat of the calorimeter and contents. These are known very approximately, and since the total correction is itself very small, the error in the determination becomes negligibly small. After the evaporation has ceased the rate of natural cooling is again measured by the Beckmann thermometer, and is usually found to be the same as before the experiment. This, combined with the time of the experiment, which is also measured, gives the second and only other correction, and it can, with careful working, be made very small. The two corrections to the latent heat combined need not exceed one calorie, and as the error in the correction cannot amount to more than about 10 per cent., the error in the latent heat through this correction cannot be more than about 0·01 per cent. The time of the experiment varies. Near the boiling point of the liquid the whole of the liquid taken has evaporated in about eight to ten minutes, but at about the ordinary temperature it requires about an hour. Of course, it makes no difference whether the time of the experiment is long or short so long as the evaporation proceeds under its own vapour pressure, which was proved by repeating some experiments at little faster rates and obtaining the same result. The expression:

$$\frac{213{\cdot}6 \times x \times V}{W} = L,$$

where $x$ is the weight of silver deposited in the voltameter, $V$ is the mean voltage, $W$ the weight of the liquid taken, and $L$ the latent heat.

*The Pure Chloroform.*—Commercially "pure" chloroform was taken, and distilled several times over an alkaline solution of potassium permanganate. It was then washed with water and dilute acid. It was dried first over calcium chloride, and then over phosphoric oxide, after which it was distilled in a fractionator and the first and last portions neglected; 700 c.c. distilled without the boiling point varying by more than 0·06°. Boiling point = 61·05°/756 mm. Specific volume at 20° = 0·67171.

*The pure benzene* was obtained by fractionating Kahlbaum's pure thiophen-free benzene over phosphoric oxide. Boiling point = 79·98°/751 mm. Specific volume at 20° = 1·13823.

The mixtures were made up by direct weighing of the constituents. The following mixtures were investigated, the compositions being always given in terms of the percentage of chloroform contained: 15·24, 29·42, 40·23, 53·04, 73·74, and 82·11. The chloroform and the mixtures were always kept in the dark, and care was taken to avoid change in composition of the mixtures through evaporation.

A series of determinations was made on the heat equivalent of the calorimeter, spiral, etc., (1) by the direct method of adding a known amount of cold water at known temperature into the calorimeter, and (2) by measuring the current required to heat the water and calorimeter through a given range of temperature which was measured on the Beckmann thermometer. The second method was found to be the best, and gave the result 46·9 calories. This quantity need not be known with any particular accuracy, a few units variation making no appreciable error in the latent heat results. Then a series of determinations was made with the water calorimeter, the latent heats of the two pure liquids and of all the above mixtures being determined over temperatures varying from 20° to 75°.

The whole series was repeated with the aniline calorimeter. In determining the correction for the difference in the initial and final temperatures of an experiment, the specific heats of aniline as found by Griffiths (*Phil. Mag.*, 1895, [v], **39**, 47) were used. Here again, however, the method of the experiments renders an accurate knowledge of the specific heats of the aniline quite superfluous.

### *Results.*

In the following tables are given the experimental values of the latent heats, together with the temperatures to which they correspond. In these tables the mixtures are given always in percentages of chloroform. Under *W* are given the results found when the calorimeter contained water, and under *A* the results when the calorimeter contained aniline. *T* is temperature, and *L* latent heat.

*Pure Benzene.*

| *W.* | | *A.* | |
|---|---|---|---|
| *T.* | *L.* | *T.* | *L.* |
| 20·5 | 104·00 | 22·7 | 103·83 |
| 29·3 | 102·77 | 43·7 | 99·86 |
| 29·0 | 102·65 | 51·5 | 99·46 |
| 28·8 | 102·96 | 59·9 | 98·29 |
| 40·1 | 101·13 | 60·7 | 98·07 |
| 52·2 | 99·14 | 69·4 | 96·68 |
| 60·9 | 97·52 | 70·6 | 95·94 |
| 68·2 | 95·97 | 74·9 | 95·43 |
| 73·4 | 95·62 | | |
| 72·9 | 95·71 | | |
| 73·0 | 95·48 | | |

*Pure Chloroform.*

| *W.* | | *A.* | |
|---|---|---|---|
| *T.* | *L.* | *T.* | *L.* |
| 20·6 | 62·85 | 22·0 | 63·09 |
| 19·3 | 63·32 | 31·8 | 62·19 |
| 21·7 | 62·55 | 43·3 | 61·05 |
| 28·57 | 62·09 | 51·5 | 60·31 |
| 29·57 | 61·85 | 52·0 | 60·20 |
| 40·4 | 61·32 | | |
| 39·8 | 61·10 | | |
| 40·0 | 61·01 | | |
| 51·9 | 60·60 | | |
| 52·6 | 60·01 | | |

15·24 *per Cent. Mixture.*

| *W.* | | *A.* | |
|---|---|---|---|
| *T.* | *L.* | *T.* | *L.* |
| 21·6 | 98·52 | 31·7 | 97·28 |
| 30·2 | 96·83 | 43·5 | 95·09 |
| 41·0 | 95·25 | 51·6 | 93·62 |
| 51·6 | 93·70 | 59·8 | 92·30 |
| 68·0 | 91·07 | 69·6 | 90·64 |
| 68·7 | 90·93 | 74·8 | 89·95 |
| 73·0 | 90·24 | | |

29·42 *per Cent. Mixture.*

| *W.* | | *A.* | |
|---|---|---|---|
| *T.* | *L.* | *T.* | *L.* |
| 19·8 | 94·20 | 22·4 | 93·84 |
| 30·2 | 92·99 | 31·9 | 92·10 |
| 40·3 | 90·86 | 43·4 | 90·61 |
| 51·6 | 88·72 | 51·6 | 88·93 |
| 68·7 | 86·55 | 59·6 | 87·60 |
| 68·0 | 85·69 | 69·9 | 85·92 |
| 72·8 | 85·79 | 74·9 | 84·81 |

40·23 *per Cent. Mixture.*

| *W.* | | *A.* | |
|---|---|---|---|
| *T.* | *L.* | *T.* | *L.* |
| 21·6 | 89·15 | 31·9 | 87·93 |
| 30·2 | 87·73 | 43·2 | 85·69 |
| 41·0 | 85·95 | 51·6 | 84·64 |
| 51·5 | 84·76 | 59·4 | 83·51 |
| 60·1 | 83·01 | 70·9 | 81·20 |
| 67·1 | 81·71 | | |

53·04 *per Cent. Mixture.*

| *W.* | | *A.* | |
|---|---|---|---|
| *T.* | *L.* | *T.* | *L.* |
| 19·9 | 82·93 | 22·6 | 82·86 |
| 30 1 | 81·98 | 31·9 | 82·94 |
| 40·7 | 80·25 | 43·1 | 80·83 |
| 40·8 | 81·04 | 54·1 | 79·01 |
| 51·5 | 79·29 | 60·0 | 78·28 |
| 59·3 | 78·58 | 70·5 | 76·98 |
| 68·4 | 77·32 | | |

73·74 *per Cent. Mixture.*

| *W.* | | *A.* | |
|---|---|---|---|
| *T.* | *L.* | *T.* | *L.* |
| 21·6 | 75·55 | 31·8 | 74·07 |
| 30·1 | 73·83 | 43·2 | 72·53 |
| 40·5 | 72·46 | 53·3 | 71·07 |
| 51·6 | 71·17 | 59·7 | 70·13 |
| 51·6 | 71·15 | 59·6 | 70·15 |
| 59·3 | 69·40 | | |

82·11 *per Cent. Mixture.*

| *W.* | | *A.* | |
|---|---|---|---|
| *T.* | *L.* | *T.* | *L.* |
| 19·8 | 71·86 | 22·2 | 71·48 |
| 30·0 | 70·28 | 31·6 | 69·71 |
| 40·2 | 68·72 | 43·1 | 68·95 |
| 52·0 | 67·80 | 52·7 | 67·90 |
| 59·5 | 67·04 | 59·5 | 67·24 |

As will be noticed, the temperatures are somewhat irregular, as it was found difficult and inconvenient to make all the determinations for each series at regular and constant temperatures. In order, therefore, to obtain comparable results and at the same time to eliminate accidental errors in the determinations, the above figures have been plotted on a large sheet of cross-section paper. First the latent heats of each mixture were plotted against the temperatures, and the smoothed curves then drawn. It was found that these curves all came out quite straight lines. The water and aniline values were used together in drawing these curves, as both series separately would give the same smoothed curve. In the following tables are given the latent heats for regular intervals of temperature as read from the smoothed curves. The values at 0° and 10°, as also the values at the higher extremes of temperature, were obtained by extrapolating the curves. This was a perfectly safe thing to do, since the curves are straight.

| Results for pure benzene. | | Griffiths and Marshall. | Results for pure chloroform. | |
|---|---|---|---|---|
| Temp. | Latent heat. | | Temp. | Latent heat. |
| 0° | 107·51 | 107·05 | 0° | 64·85 |
| 10 | 105·89 | 105·47 | 10 | 63·95 |
| 20 | 104·26 | 103·89 | 20 | 63·06 |
| 30 | 102·65 | 102·22 | 30 | 62·17 |
| 40 | 101·05 | 100·71 | 40 | 61·29 |
| 50 | 99·44 | 99·14 | 50 | 60·40 |
| 60 | 97·84 | 97·56 | 60 | 59·51 |
| 70 | 96·23 | 96·00 | 61·27 | 59·40 |
| 80 | 94·61 | 94·40 | | |
| 80·3 | 94·55 | 94·37 | | |

For comparison the results by Griffiths and Marshall (*loc. cit.*) for pure benzene are also given. It will be noticed that our results are a little higher. The values at the boiling points (at 760 mm.) have been obtained by extrapolation. The boiling-point result for chloroform compares very well with the result 59·29 at 61·52° (=59·31 at 61·27°) found by one of us (T., 1911, **99**, 1633) by an entirely different method.

The probable error of the results we consider not in general to be higher than ±0·1 calories. In the following tables are given the results for the various mixtures investigated.

| Temperature. | Latent heat. | | | | | |
|---|---|---|---|---|---|---|
| | 15·24%. | 29·42%. | 40·23%. | 53·04%. | 73·74%. | 82·11% of $CHCl_3$. |
| 0° | 102·13 | — | — | — | 78·53 | — |
| 10 | 100·49 | 96·03 | 91·12 | — | 77·09 | 72·66 |
| 20 | 98·89 | 94·34 | 89·55 | 83·12* | 75·65 | 71·50 |
| 30 | 97·20 | 92·62 | 87·97 | 81·93* | 74·21 | 70·37 |
| 40 | 95·55 | 90·91 | 86·38 | 80·71* | 72·79 | 69·24 |
| 50 | 93·93 | 89·26 | 84·80 | 79·49* | 71·41 | 68·14 |
| 60 | 92·32 | 87·63 | 83·19 | 78·28 | 70·05 | 67·06 |
| 70 | 90·72 | 85·57 | 81·57 | 77·09 | 68·70 | 65·98 |
| 80 | 89·13 | — | — | 75·88 | 67·37 | — |

* These results are probably slightly low.

Latent heats were next plotted against composition for each constant temperature. The curves obtained showed only slight curvature. From these curves values were read off at even composition. They are given in the following table:

| Composition. | Latent heats at | | | | | |
|---|---|---|---|---|---|---|
| | 20°. | 30°. | 40°. | 50°. | 60°. | 70°. |
| 10% $CHCl_3$ ... | 100·75 | 99·25 | 97·55 | 95·98 | 94·44 | 92·60 |
| 20% $CHCl_3$ ... | 97·32 | 95·79 | 94·00 | 92·45 | 90·80 | 89·05 |
| 30% $CHCl_3$ ... | 93·82 | 92·28 | 90·43 | 88·81 | 87·26 | 85·65 |
| 40% $CHCl_3$ ... | 90·00 | 88·46 | 86·63 | 84·98 | 83·45 | 81·76 |
| 50% $CHCl_3$ ... | 85·98 | 84·44 | 82·70 | 81·13 | 79·55 | 78·05 |
| 60% $CHCl_3$ ... | 81·78 | 80·20 | 78·67 | 77·15 | 75·70 | 74·29 |
| 70% $CHCl_3$ ... | 77·32 | 75·85 | 74·47 | 73·07 | 71·70 | 70·50 |
| 80% $CHCl_3$ ... | 72·68 | 71·34 | 70·18 | 68·94 | 67·70 | — |
| 90% $CHCl_3$ ... | 67·92 | 66·76 | 65·78 | 64·72 | 63·66 | — |

In the previously mentioned investigation by one of us on the latent heats of mixtures of chloroform and benzene results were given for a series of temperatures which were the boiling points of the mixtures at pressures fairly near 760 mm. By extrapolating the values given in the above table we can obtain the latent heats at the boiling points, and thus compare them with the values previously obtained.

| Composition. | Temperature. | $L$. | $L'$. |
|---|---|---|---|
| 10% $CHCl_3$ ......... | 79·86° | 91·31 | 91·1 |
| 20% $CHCl_3$ ......... | 79·03 | 87·57 | 87·9 |
| 30% $CHCl_3$ ......... | 78·13 | 84·36 | 84·6 |
| 40% $CHCl_3$ ......... | 77·15 | 80·46 | 81·4 |
| 50% $CHCl_3$ ......... | 75·95 | 77·16 | 78·2 |
| 60% $CHCl_3$ ......... | 74·60 | 73·48 | 75·0 |
| 70% $CHCl_3$ ......... | 72·84 | 69·96 | 71·6 |
| 80% $CHCl_3$ ......... | 70·48 | 66·40 | 68·3 |
| 90% $CHCl_3$ ......... | 67·00 | 63·00 | 64·4 |
| 100% $CHCl_3$ ......... | 61·45 | 59·38 | 59·29 |

The temperatures given in the second column of the above table were obtained from previous work. The values under $L$ are the latent heats at these temperatures, and the values under $L'$ the latent heats determined in previous work. An exact agreement between the two sets of values is not expected because the previously obtained results represent the latent heat plus a small extra quantity of heat required to expand the vapour from the volume at the vapour pressure of the mixture at the temperature considered, to the volume at the atmospheric pressure, work being done against the atmospheric pressure. The previously determined results should therefore be slightly greater than those determined by the extrapolation of the results obtained in the present work.

### *Discussion of Results.*

The complete set of values of the latent heat of chloroform and benzene mixture enable us to answer the following questions:

(1) How does the latent heat of a mixture of two normal liquids vary with the temperature?

(2) How does the latent heat of a mixture vary with the composition when the temperature is constant?

In regard to the first question we may state at once *that the latent heat at constant composition of a mixture of two normal liquids is, at least for temperatures at which the vapour pressure is less than atmospheric, a linear function of the temperature.* In this respect, therefore, a mixture behaves exactly like a pure liquid. With regard to question (2) it was found on plotting the curves that they were very nearly straight lines. They were all just slightly concave to the composition axis. The deviation from the additive or linear function is shown by the following table, which contains under $L$ the observed latent heats and under $L$ (cal.) the latent heats calculated according to the linear function from the latent heats of the pure constituents at the same temperature. Under $\Delta$ are given the differences or deviations from the additive.

| Temperature. | Composition. | *L.* | *L* (cal.). | Δ. |
|---|---|---|---|---|
| 20° | 10% $CHCl_3$ | 100·75 | 100·23 | +0·52 |
| | 30% $CHCl_3$ | 93·82 | 92·17 | +1·65 |
| | 50% $CHCl_3$ | 85·98 | 84·11 | +1·87 |
| | 70% $CHCl_3$ | 77·32 | 76·05 | +1·27 |
| | 90% $CHCl_3$ | 67·92 | 67·99 | −0·07 |
| 40° | 10% $CHCl_3$ | 97·55 | 97·61 | −0·06 |
| | 30% $CHCl_3$ | 90·43 | 89·52 | +0·91 |
| | 50% $CHCl_3$ | 82·70 | 81·43 | +1·27 |
| | 70% $CHCl_3$ | 74·47 | 73·34 | +1·13 |
| | 90% $CHCl_3$ | 65·78 | 65·24 | +0·54 |
| 60° | 10% $CHCl_3$ | 94·45 | 94·01 | +0·44 |
| | 30% $CHCl_3$ | 87·26 | 86·34 | +0·92 |
| | 50% $CHCl_3$ | 79·55 | 78·68 | +0·87 |
| | 70% $CHCl_3$ | 71·70 | 71·01 | +0·69 |
| | 90% $CHCl_3$ | 63·66 | 63·35 | +0·31 |

The deviations, it will be noticed, are only small, and seem to become smaller as the temperature rises. We may state, then, that *the latent heat of a mixture of two normal liquids at constant temperature is approximately a linear function of the composition.* Probably with absolutely normal liquids the agreement with the additive law will be exact, and with less normal liquids, and particularly with liquids which form compounds or solvates when mixed, the deviations will probably be strongly marked.

Although these generalisations are based on one pair of liquids only there can be little doubt that these are quite normal, and form normal mixtures typical of this class of liquid. Moreover, one of the authors has already shown in previous work that the latent heats of the chloroform benzene mixtures at their boiling points show the same simple behaviour as do other mixtures (T., 1912, **101**, 81).

The latent heats considered in this work consist, in part, like the ordinary latent heats of pure liquids, of external work done in the vaporisation.

Sufficient data are not available for the calculation of this external work, but in any case it is comparatively small, and does not vary greatly from one liquid to another, so that the generalisations arrived at will be scarcely affected by taking the external work into account.

It may be added finally that now the additive nature of latent heats for mixtures is established, the method of detecting solvates in mixtures of liquids described by one of us (T., 1912, **101**, 1104) may be applied to results for mixtures at constant temperature.

### *Summary.*

A method is described for accurately determining latent heats at constant composition of mixtures over a large temperature range.

The latent heats of pure chloroform and pure benzene, and mixtures of these liquids of varying compositions, have been determined between the ordinary temperature and the boiling points.

It is found that for any given mixture the latent heat is a linear function of the temperature, and for a given temperature the latent heat is approximately a linear function of the composition.

In conclusion, the authors thank the Chemical Society for a research grant, which has largely defrayed the cost of the work.

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# LIX.—*The Relation Between the Absorption Spectra of Acids and their Salts. Part I. Sodium Salts.*

By Robert Wright (1851 Exhibition Scholar).

It is a matter of common knowledge that many acids show a marked colour change when their acidic hydrogen is replaced by a metal, such as sodium, which in itself is colourless. The various indicators used in acidimetry, for example, litmus or methyl-orange, furnish well-known examples of such phenomena. By the application of photography the investigations have been extended to the invisible regions of the spectrum, with the result that numerous substances (such as the phenols) are now known which show a marked change in their absorption spectra on the addition of sodium hydroxide. This change is most frequently ascribed to a variation in molecular structure taking place on salt-formation; the present investigations, however, seem to indicate that change in absorptive power can occur where such variation is hardly possible.

For the most part the examination has been confined to acids of a simple structure, where there is little possibility of atomic rearrangement taking place on neutralisation. Further, aqueous solutions were used throughout, so that any change in absorptive power which might be produced by alteration of the degree of ionisation would have its full effect. As many of the substances photographed have been previously investigated, the full absorption curves have not been drawn, but the results are expressed by means of tables.

*The Fatty Acids.*—As will be seen from the table, these acids all show a decrease in absorptive power on salt-formation. This decrease is most marked in the case of formic acid, and grows less as we ascend the series. In the case of the substituted acetic acids, the spectra of salt and acid were practically identical. In this table, as in all others, the ionisation constant $k$ of each acid is given; these constants were obtained from Kohlrausch's "Leitvermögen der Elektrolyte." The limits of absorption for 10 cm. and 1 cm. are given in wave-lengths.

TABLE I.

| | 10 cm. Spectrum transmitted to λ. | 1 cm. Spectrum transmitted to λ. | κ. |
|---|---|---|---|
| Formic acid, $N$ | 2520 | 2430 | 0·0214 |
| Sodium formate, $N$ | 2430 | 2330 | — |
| Acetic acid, $N$ | 2460 | 2355 | 0·0018 |
| Sodium acetate, $N$ | 2410 | 2320 | — |
| Propionic acid, $N$ | 2480 | 2360 | 0·0013 |
| Sodium propionate, $N$ | 2460 | 2335 | — |
| *n*-Butyric acid, $N$ | 2500 | 2380 | 0·0015 |
| Sodium *n*-butyrate, $N$ | 2480 | 2340 | — |
| *iso*Valeric acid, $N/10$ | 2560 | 2390 | 0·0017 |
| Sodium *iso*valerate, $N/10$ | 2520 | 2330 | — |
| Chloroacetic acid, $N$ | 2620 | 2500 | 0·155 |
| Sodium chloroacetate, $N$ | 2610 | 2490 | — |
| Trichloroacetic acid, $N$ | 2730 | 2590 | 121 (?) |
| Sodium trichloroacetate, $N$ | 2730 | 2590 | — |
| Phenylacetic acid, $N/100$ | 2695 | 2330 | 0·0056 |
| Sodium phenylacetate, $N/100$ | 2700 | 2330 | — |

Trichloroacetic acid and its salt were also photographed in more dilute solutions, and their spectra remained identical down to 1 cm. of $N/100$-solution.

*The Dibasic Acids.*—In this series, as in the fatty, the change is most marked in the lower members, having almost disappeared in the case of succinic acid. In the neutralisation of $N$-oxalic acid, potassium was used instead of sodium, as the oxalate of the latter is not sufficiently soluble; both metals were examined in $N/10$-solution, the two spectra being almost identical. Fumaric acid was examined in order to see if the property of simple unsaturation produced any effect; it will be noted that both acid and salt have the same absorptive power. Calcium malonate and calcium succinate were also photographed, the former in $N/100$- and the latter in $N/10$-solution; it being thought that in these cases the presence of a bivalent metal might give rise to a cyclic compound. Unfortunately at the dilutions used both salts are practically diactinic, so that, even if a ring is formed, it produces no increase in absorptive power, at any rate in aqueous solutions.

It is interesting to note that whilst conjugation of unsaturated centres does not of necessity induce change in absorptive power on salt-formation, still the view put forward in two former papers (Crymble, Stewart, Wright, Rea, and Glendinning, T., 1911, **99**, 541, 1262)—that greater general absorption is shown by compounds possessing such conjugation than by those in which it is absent—finds strong confirmation in the results obtained for this series. Of the first three members oxalic acid shows the greatest absorption, and succinic the least, proving that the effect of conjugation can outweigh that of increasing molecular weight.

TABLE II.

| | 10 cm. Spectrum transmitted to λ. | 1 cm. Spectrum transmitted to λ. | κ. |
|---|---|---|---|
| Oxalic acid, *N* .................. | 3000 | 2800 | 10·0 (?) |
| Potassium oxalate, *N* ......... | 2860 | 2680 | — |
| Malonic acid, *N*.................. | 2520 | 2440 | 0·163 |
| Sodium malenate, *N*........... | 2485 | 2385 | — |
| Succinic acid, *N*.................. | 2460 | 2350 | 0·0066 |
| Sodium succinate, *N*........... | 2460 | 2340 | — |
| Fumaric acid, *N*/100........... | 3005 | 2720 | 0·09 |
| Sodium fumarate, *N*100 ...... | 3000 | 2720 | — |

More dilute solutions were examined in the cases of oxalic and fumaric acids, the results being in harmony with those obtained for the higher concentrations.

*Various Aromatic Acids.*—Acids which contain an aromatic nucleus often exhibit a greater change in absorptive power on neutralisation than do those of an aliphatic nature. The indicators, and the "pseudo-acids" of Hantzsch, all possess this property in a marked degree; fundamental difference of structure between the acid and its salt being in these cases the generally accepted explanation. Numerous compounds of a phenolic nature, as investigated by Baly and others (T., 1905, **87**, 1345; 1910, **97**, 1494) also show considerable change on the addition of sodium hydroxide, but the cause of the change is not quite so evident. Finally, there are many acids of an aromatic nature the spectra of which are either identical with those of their sodium salts, or else differ from the latter only in a very slight degree. In this last group we may place benzoic acid, and the homologous compounds, phenylacetic and phenylpropionic acid. The following table contains the results for a few of the more simple compounds photographed in aqueous solutions.

### TABLE III.

| | 10 cm. Spectrum transmitted to λ. | 1 cm. Spectrum transmitted to λ. | κ. |
|---|---|---|---|
| Benzoic acid, *N*/100 | 2935 | 2875 | 0·0060 |
| Sodium benzoate, *N*100 | 2865 | 2790 | — |
| Phenylacetic acid, *N*/100 | 2695 | 2330 | 0·0056 |
| Sodium phenylacetate, *N*/100 | 2700 | 2330 | — |
| Phenylpropionic, *N*/100 | 2710 | 2310 | 0·0023 |
| Sodium phenylpropionate, *N*/100 | 2710 | 2300 | — |
| Cinnamic acid, *N*/1000 | 3190 | 3100 | 0·0035 |
| Sodium cinnamate, *N*/1000 | 3090 | 3005 | — |
| Salicylic acid, *N*/100 | 3400 | 3320 | 0·102 |
| Sodium salicylate, *N*100 | 3490 | 3350 | — |
| Phenol, *N*/10 | 2920 | 2875 | very small |
| Sodium phenoxide, *N*/10 | 3180 | 3135 | — |
| Picric acid, *N*/10,000 | 4350 | 2320 | very great |
| Sodium picrate, *N*/10,000 | 4350 | 2320 | — |
| Hippuric acid, *N*/100 | 2895 | 2820 | 0·0222 |
| Sodium hippurate, *N*/100 | 2890 | 2820 | — |

The absorption bands which exist in phenol and its derivatives have been left out of account in the above table; also, most of the compounds were examined in more dilute solutions, the results being in agreement with those given.

*Inorganic Acids.*—For the most part the inorganic acids are unsuitable for this type of investigation, for since the property of homology is absent, it is not possible to draw comparisons between acids of gradually varying structure; moreover, a considerable number of the inorganic acids and salts are too diactinic to admit of investigation. Mention should be made of the work of Hartley, who has shown that nitric acid and its potassium salt give identical spectra (T., 1902, **81**, 556), whilst Ostwald has made a large number of experiments with the permanganates and other coloured salts.

Two cases of interest will be mentioned out of the few acids examined. Hydrogen sulphide and arsenious acid both show a large increase in absorption on neutralisation with sodium hydroxide.

### TABLE IV.

| | Acid. | | Salt. | |
|---|---|---|---|---|
| | 10 cm. | 1 cm. | 10 cm. | 1 cm. |
| Hydrogen sulphide, *N*/10 | 2480 | 2330 | 2790 | 2685 |
| Arsenious acid, *M*/10 | 2435 | 2320 | 2695 | 2570 |

## EXPERIMENTAL.

The water used in this investigation was distilled from silica, the vapour being passed over red-hot silica wool. A sample of 10 cm. thickness was diactinic to $\lambda=2260$.

As a rule, the salts were prepared by the addition of excess of sodium hydroxide to the acid. The sodium hydroxide used was prepared from metallic sodium. A 10 cm. length of $2N$-solution was diactinic to $\lambda=2330$. The substances used were purified so as to give constant melting or boiling points. The hydrogen sulphide was prepared from iron sulphide, and was purified by passing the dry gas over iodine; it was then well washed before being absorbed. The strength of the solution was estimated by means of iron alum and potassium permanganate.

In every case the acid and its salt were photographed on the same plate, thus avoiding errors due to difference of development; moreover, various other thicknesses were examined besides those tabulated.

### *Summary.*

Although it is hardly possible with the present data to state definitely when an acid will show an absorption spectrum different from that of its sodium salt; still, the following points seem clear.

1. The change in degree of ionisation which takes place on the neutralisation of an acid does not in itself of necessity produce a change in the absorption spectrum.

2. Many acids show spectra differing from those of their sodium salts, even when the structure of the acid is so simple as to scarcely admit of molecular rearrangement.

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## LX.—*Metaphosphoric Acid and its Alkali Salts.**

By ALFRED HOLT and JAMES ECKERSLEY MYERS.

AT least six series of metaphosphates have been described by various investigators. They are supposed to be derived from a corresponding series of acids, but the evidence for their constitution depends either on the method of preparation or empirical composition, for being mainly insoluble substances, little or nothing is known as to their molecular weights.

* For abstract, see P., 1913, **29**, 61.

Metaphosphoric acid, obtained either by dehydrating the ortho-acid or by treating phosphoric oxide with moist air, has been found by Tilden and Barnett to possess when in a state of vapour a molecular weight corresponding with the formula $(HPO_3)_2$, and we have already shown (T., 1911, **99**, 384) that from freezing-point determinations the ordinary glacial sticks when in solution probably consist of termolecular complexes, whilst the acid obtained by decomposition of lead metaphosphate is present in single molecules. We have also described three varieties of the meta-acid, each characterised by its behaviour towards water. The present communication contains a re-examination of many of these points.

The first series of experiments was directed towards the changes produced by heat on the density and composition of commercial metaphosphoric acid.

| Composition, per cent. | Length of heating, in hours. | Density.* | Loss in weight between each heating, per cent. | Total loss in weight, per cent. | Behaviour on solution. |
|---|---|---|---|---|---|
| 74·2 $P_2O_5$<br>= 83·87 $HPO_3$<br>16·13 $H_2O$ | — | 1·214 | — | — | Readily soluble |
| 77·7 $P_2O_5$<br>= 89·29 $HPO_3$<br>10·71 $H_2O$ | 4 | 1·350 | 4·5 | 4·5 | Dissolves easily with crackling |
| 78·7 $P_2O_5$<br>= 89·9 $HPO_3$<br>10·1 $H_2O$ | 5½ | 1·356 | 6·28 | 10·78 | Soluble with difficulty, crackles |
| 78·7 $P_2O_5$<br>= 89·9 $HPO_3$<br>10·1 $H_2O$ | 6½ | 1·404 | 7·6 | 18·38 | ,, ,, |

* The values previously given (T., 1911, **99**, 390, 391) should be 1·488 and 1·216 instead of 2·488 and 2·216 respectively.

The heating was carried out in a platinum dish over an efficient Méker burner, and it will be seen from the above data that once the glass has attained a composition of about 78 per cent. of phosphoric oxide no great change occurs in the composition of the glass or vapour. The rate of volatilisation of the glass was about 0·1 gram per hour at the temperature of the experiment. This constancy of composition (78·7 per cent. of phosphoric oxide) is lower than is required theoretically for metaphosphoric acid (88·7 per cent.) and is still lower than the value of Tilden and Barnett.

This low percentage of phosphoric oxide could be accounted for by the presence of a small quantity of sodium metaphosphate, a very common impurity in ordinary glacial acid. If a sodium salt, which is not volatile, was present, the percentage of phosphoric oxide in the glass should diminish as the acid was volatilised away, but as 7·6 per cent. of glass can be thus removed with no change in composition, the presence of a sodium salt is improbable. It is noticeable that this low value for the phosphoric oxide content is nearly that required for pyrophosphoric acid (79·7 per cent.), and hence it might very reasonably be concluded that the heating had been insufficient to do more than form the pyro-acid, and that this, like the meta-variety, is somewhat volatile.

The objections to this view are that the reactions of a solution of this glass in water are not those of pyrophosphoric acid, that it was prepared by heating a substance (glacial acid), which showed the reactions of metaphosphoric acid, and that the precipitate obtained by adding barium chloride to a solution of the glass in water gave a ratio:

$$\frac{\text{Ba precipitate}}{BaSO_4} = 1{\cdot}349,$$

the theoretical value for $Ba(PO_3)_2$ being 1·266. These values are in fair agreement, particularly as the determined ratio is too high, for the presence of any other phosphate would lower it.

The freezing points of solutions of these acids in water were also examined, and the results are contained in the annexed table:

| Composition of acid, per cent. | Strength of solution in grams per 100 c.c. | Mol. wt. calculated from freezing point. |
|---|---|---|
| 74·2 $P_2O_5$ .................. | 6·7 | 198 |
| 74·2 $P_2O_5$ .................. | 3·32 | 185 |
| 74·2 $P_2O_5$ .................. | 0·67 | 138 |
| 77·7 $P_2O_5$ .................. | 4·63 | 123 |
| 77·7 $P_2O_5$ .................. | 1·93 | 156 |
| 78·7 $P_2O_5$ .................. | 3·47 | 170 |

From these values it is probable that the acid is present in solution as termolecular complexes more or less dissociated. It is true that these values would equally well agree with the molecular weight of pyro-acid (178), but reasons have been given which render the presence of this compound very unlikely.

The acid obtained by decomposing lead metaphosphate gives different results.

The lead salt was prepared by the action of lead acetate solution on a solution of glacial phosphoric acid exactly neutralised by potassium hydroxide, and had the empirical composition $Pb(PO_3)_2$. It was decomposed with hydrogen sulphide, and a solution containing 3·272 grams of metaphosphoric acid per 100 c.c. was prepared. This gave a freezing point in agreement with a molecular weight of 73. $HPO_3$ requires M.W. = 80.

A portion of this solution was then evaporated to dryness, and the resulting glass cautiously heated to redness. After cooling it was dissolved in just so much water as again to yield a solution containing 3·272 grams per 100 c.c. This solution now gave a freezing point from which the molecular weight is calculated to be 172. One can therefore conclude that monometaphosphoric acid can only be obtained in solution, any attempt at evaporation producing polymerisation.

It is of interest to compare the changes in the depression of the freezing point of these two varieties of acid on hydration.

In the following table values are given for solutions of equal strength, but consisting of the mono- and tri-acids respectively. It will be seen that little change takes place in the mono-acid, whilst there is a progressive change in the other case.

| | Depression of freezing point. | |
|---|---|---|
| Time in days. | Mono-acid. | Tri-acid. |
| 1 | 0·85 | 0·36 |
| 2 | 0·85 | 0·51 |
| 4 | 0·86 | 0·66 |
| 15 | 0·88 | 0·76 |
| 60 | 0·89 | 0·89 |

Hence it may be concluded, as pointed out in our previous paper, that the hydration of monometaphosphoric acid proceeds in a direct (unimolecular) manner, whilst in the case of the tri-acid no such simple change takes place, for the change $HPO_3,H_2O = H_3PO_4$ would only affect the depression of the freezing point by reason of the difference in dissociation of the two acids.

When a solution of this mono-acid is exactly neutralised with sodium hydroxide, no precipitation takes place. It is usually stated that alkaline monometaphosphates are insoluble, so it is clear in this case that either this statement is incorrect, or else that mono-acid, on neutralisation, does not yield a mono-salt. The freezing point of this neutral solution was therefore taken, and was found to agree with a molecular weight of 102 ($NaPO_3$). Sodium monometaphosphate can be obtained in a crystalline condition by heating sodium ammonium hydrogen orthophosphate until a clear glass is obtained. When this is slowly cooled it crystallises, but it is usually easier to reheat the glass after it has been allowed to cool completely.

Two solutions, one of the glass, and the other of the crystals obtained by devitrifying it, were prepared, and their freezing points determined:

| Strength and nature of solution. | Depression of freezing point. | Mol. weight. |
|---|---|---|
| 2·77 grams of crystals in 100 c.c. ...... | 0·51 | 103 |
| 2·643 ,, glass in 100 c.c. ......... | 0·14 | 348 |
| 0·491 ,, ,, ,, ......... | 0·04 | 233 |

It may therefore be concluded that the crystals are monometaphosphate, and the glass at least termolecular complexes, and that these dissociate considerably in dilute solution.

Attempts to prepare dimetaphosphates have not been successful. When orthophosphoric acid was heated with the oxides of zinc or copper, and the resulting mass decomposed by the action of an alkaline sulphide, the addition of alcohol precipitated a gelatinous substance which it was found almost impossible to free from the rest of the solution. When filtered and dried as well as possible it was found to contain 43 to 45 per cent. of phosphoric oxide, which is too low a value for any simple alkaline phosphate. The sodium salt prepared from zinc oxide and orthophosphoric acid appeared to have a molecular weight in solution of about 154, whilst that of the corresponding potassium salt from the copper compound was about 339. They are therefore probably mixtures of sodium salts and phosphoric acids, and not definite compounds.

### *Conclusions.*

1. The hydration of metaphosphoric acid is unimolecular when the acid is present in solution in simple molecules.
2. Alkaline monometaphosphates are soluble in water.
3. The alkaline metaphosphates appear to be derived from mono- and tri-metaphosphoric acid.

THE UNIVERSITY,
MANCHESTER.

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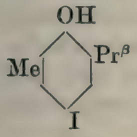
## LXI.—*The Action of Chlorine on Thymol and on* m-*Cresol.*

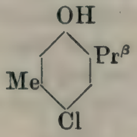
By HORACE LESLIE CROWTHER and HAMILTON MCCOMBIE.

IN continuation of the study of the action of chlorine on iodophenols (Brazier and McCombie, T., 1912, **101**, 968; King and McCombie, T., 1913, **103**, 220), the authors investigated the action of chlorine on 6-iodothymol (I). It was found that this compound, on chlorination in carbon tetrachloride solution, readily lost iodine, and after chlorination for one to two hours, a compound, $C_{10}H_9OCl_5$, was obtained. On chlorination for a further period, a substance was obtained which proved to be a derivative of *m*-cresol. As the iodine was so easily displaced by chlorine from 6-iodothymol (I), the process evidently resolved itself into a chlorination of thymol in the presence of iodine, and, since not only thymol derivatives resulted, but also *m*-cresol compounds, the authors have investigated the action of chlorine on these two substances, under different conditions of temperature, in different solvents, and in the presence of several catalysts.

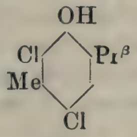
Very little seems to have been done with regard to the chlorination of thymol. By the action of sulphuryl chloride on thymol, Bocchi (*Gazzetta*, 1897, **26**, ii, 403) and Peratoner and Condorelli (*ibid.*, 1899, **28**, i, 214) were able to prepare 6-chlorothymol (II); the same compound has also been obtained by Robertson and Briscoe (T., 1912, **101**, 1968) by the direct action of the theoretical quantity of chlorine on thymol. Blum (*Zeitsch. physiol. Chem.*, 1892, **16**, 518), by boiling 2: 6-dichlorothymolglycuronic acid with sulphuric acid, isolated 2: 6-dichlorothymol (III). In a paper entitled "Etudes sur l'essence de thym," Lallemand (*Ann. Chim. Phys.*, 1857, [iii], **49**, 148) describes a trichloro- and a pentachlorothymol, both of which he obtained by the direct chlorination of thymol. The pentachloro-compound is described as decomposing at 200° with the formation of propylene and tetrachloro-*m*-cresol.



(I.)

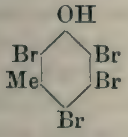


(II.)

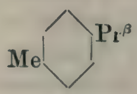


(III.)

Several benzenoid compounds, containng the *iso*propyl group, on chlorination and bromination, appear to lose that group very easily. Thus Dahmer, in a paper on the nitration of bromophenols (*Annalen*, 1904, **333**, 346), found it impossible to introduce more than two atoms of bromine into the thymol molecule, even by acting on it with a large excess of bromine. The product which he obtained, employing excess of bromine, was 2: 4: 5: 6-tetrabromo-*m*-cresol (IV). A similar elimination of the *iso*propyl group was also noticed by Arnand (*Compt rend.*, 1898, **126**, 1284). This experimenter found that cymene (V), on bromination in the presence of aluminium bromide, gave rise to pentabromotoluene (VI), whilst thymol under similar conditions yielded 2: 4: 5: 6-tetrabromo-*m*-cresol (IV).



(IV.)



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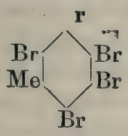
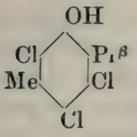


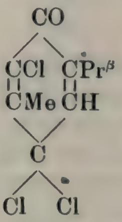
(VI.)

## 1. *Direct Chlorination of Thymol.*

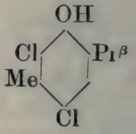
If solid thymol is subjected to the action of chlorine, it is at once attacked with the evolution of much hydrogen chloride. The thymol is liquefied by the great amount of heat evolved, and the colour of the solution changes to dark red, which gradually lightens on continued chlorination. Finally, a yellow, crystalline substance is obtained, which is identical with the compound described by Lallemand (*loc. cit.*) as 2 : 5 : 6-trichlorothymol (VII). From the fact that this trichloro-compound did not dissolve in sodium hydroxide, but was slowly decomposed by it on warming, and, from the further fact that no acyl derivatives of it could be obtained, it was suspected that this substance was not trichlorothymol, but was 2 : 4 : 4-trichloro-3-methyl-6-*iso*propyl-$\Delta^{2:5}$-*cyclo*hexadienone (VIII). A further argument for this constitution of the substance is furnished by its behaviour towards potassium iodide. If the compound is treated with potassium iodide in acetic acid solution, iodine is at once liberted, and the reaction can be followed quantitatively by titrating the iodine liberated with *N*/10-sodium thiosulphate. It was found that two atoms of iodine were liberated for every molecule of the trichloro-compound, and the equation representing the transformation is as follows:



(VII.)



(VIII.)



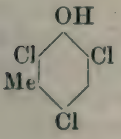
(III.)

$$C_{10}H_{11}OCl_3 + 2KI = C_{10}H_{11}Cl_2OK + KCl + I_2.$$

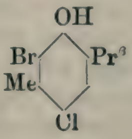
From the potassium salt of the dichlorothymol which is produced in this reaction, the acetic acid forms the free phenol (III), and, when the reaction mixture is poured into water, this compound separates as an oil. This compound is probably identical with the dichlorothymol described by Blum (*loc. cit.*), although the latter gives no boiling point for his compound. In contradistinction to the dichloro-compound, 2 : 6-dichlorothymol is readily soluble in potassium hydroxide, and, with methyl sulphate, yields a methyl derivative, thus establishing the existence of a hydroxyl group in its molecule. By leading chlorine into the oily 2 : 6-dichlorothymol, hydrogen chloride is evolved, and the trichloro*cyclo*hexadienone is regenerated.

The so-called trichlorothymol is described, both in Beilstein's "Handbuch," and in Richter's "Lexikon," as forming an isomeric compound on treatment with sulphuric acid at 100°. This appears to be a mistake, for, on referring to Lallemand's original paper, we find the statement made by him is that the trichlorothymol is transformed by the action of sulphuric acid at 100° into "l'acide phénique trichloré." The authors have repeated this reaction, and have found that the trichloro-compound was very easily decomposed by sulphuric acid at 100°, little or no charring took place, and the resulting compound was 2 : 4 : 6-trichloro-*m*-cresol (IX). This compound is dealt with later under the chlorination of *m*-cresol. The melting point of the "isomeric trichlorothymol" mentioned in Beilstein and of Lallemand's "acide phénique trichloré" agrees well with that obtained by the authors for trichloro-*m*-cresol, namely, 46°.

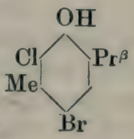
This formation of trichloro-*m*-cresol by the action of sulphuric acid on trichloromethyl*iso*propyl*cyclo*hexadienone (VIII) must be brought about by the elimination of the *iso*propyl group and the migration of one of the chlorine atoms into the position occupied by the *iso*propyl group. A somewhat similar migration of halogen atoms in the thymol series has been noticed by Robertson and Briscoe (*loc. cit.*), who have shown that 6-chlorothymol (II), on bromination, yields a mixture of 6-chloro-2-bromothymol (X) and 2-chloro-6-bromothymol (XI). To explain this, these authors assume that an intermediate compound (XII) is formed, and that then the halogen wanders.



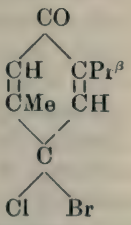
(IX.)



(X.)



(XI.)

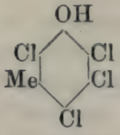


(XII.)

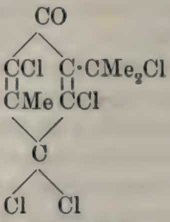
The chlorination of thymol in carbon tetrachloride solution did not proceed very far, for the resulting product was an oil, probably dichlorothymol. From this yellow oil there separated sometimes, after the solution had remained for a long time, a few crystals of the trichloro-compound. Without the presence of a catalyst, the chlorination could, under no conditions, be carried further than the trichloro-compound.

### 2. *Chlorination of Thymol in Presence of Iodine.*

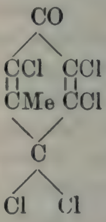
If thymol is chlorinated for several hours at the ordinary temperature, in dilute carbon tetrachloride or acetic acid solution, the first product that can be isolated is a small quantity of a pentachloro-compound. This product, on gently warming in acetic acid or alcoholic solution, slowly liberated iodine from potassium iodide, but it was found impossible to follow the reaction quantitatively. The pentachloro-compound was insoluble in potassium hydroxide, and formed no acetyl or benzoyl derivatives. It was decomposed by concentrated sulphuric acid at 150—200°, with much charring and the formation of a small quantity of tetrachloro-*m*-cresol (XIII). These reactions are analogous to those of the trichloro-compound, and the pentachloro-compound is most probably 2 : 4 : 4 : 5-tetrachloro-3-methyl-6-β-chloro*iso*propyl-$\Delta^{2:5}$-*cyclo*hexadienone (XIV).



(XIII.)



(XIV.)



(XV.)

It was found to be almost impossible to arrest the chlorination at the stage of the production of this pentachloro-compound, especially in more concentrated solutions, as the *iso*propyl group was very readily eliminated with the production of *m*-cresol derivatives. The next product which was formed after the pentachloro-compound was 2 : 4 : 5 : 6-tetrachloro-*m*-cresol (XIII), which separated from the concentrated carbon tetrachloride solution. This substance yielded both an acetyl and a benzoyl derivative, thus showing the presence of a hydroxyl group in the molecule; the compound did not liberate iodine from potassium iodide.

Tetrachloro-*m*-cresol is mentioned by Lallemand as being formed by the decomposition of pure pentachlorothymol, but the melting point of it, as given by that experimenter, appears to be very low.

Tetrachloro-*m*-cresol, on chlorination in carbon tetrachloride solution, in the presence of iodine, passed very readily into 2 : 4 : 4 : 5 : 6-pentachloro-3-methyl-$\Delta^{2:5}$-*cyclo*hexadienone (XV), which was found to be the chief and final product of the complete chlorination of thymol in the presence of iodine. The constitution of this compound was established by reactions similar to those employed in the case of 2 : 4 : 4-trichloro-3-methyl-6-*iso*propyl-$\Delta^{2:5}$-*cyclo*hexadienone (VIII). It liberated iodine very readily from potassium iodide in alcoholic or acetic acid solution, and, by titrating the iodine thus liberated, the reaction was followed quantitatively, and was found to agree with the following equation:

$$C_7H_3OCl_5 + 2KI = C_7H_3Cl_4OK + KCl + I_2.$$

No acetyl or benzoyl derivatives could be obtained from this substance, and the compound was easily attacked and decomposed by alkalis. On treatment with concentrated sulphuric acid at 100°, 2 : 4 : 4 : 5 : 6-pentachloro-3-methyl-$\Delta^{2:5}$-*cyclo*hexadienone was oxidised very readily to 2 : 4 : 5-trichlorotoluquinone (XVI). The identity of this last compound was established by a mixed melting-point determination with a specimen of the trichlorotoluquinone prepared by the oxidation of *o*-toluidine with sodium dichromate (compare Elbs and Brunschweiler, *J. pr. Chem.*, 1896, [ii], **52**, 539). Small quantities of 2 : 4 : 5-trichlorotoluquinone were also obtained by the prolonged chlorination (lasting for about ten days) of thymol in presence of iodine, in carbon tetrachloride solution.

### 3. *Chlorination of Thymol in the Presence of Reduced Iron.*

In the hope of obtaining better yields of the pentachloro-derivative from thymol, the chlorination was carried out in the presence of a small quantity of reduced iron. The iron, however, seemed to have a much greater catalytic effect than the iodine. The solution to be chlorinated was a solution of thymol in carbon tetrachloride, a little reduced iron was added, and the mixture was cooled in a freezing mixture. The following results were obtained:

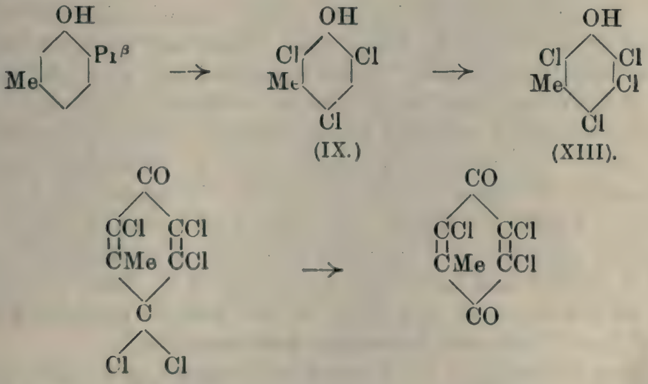
After twenty minutes, an oil.

After three-quarters to one and a-half hours, 2 : 4 : 6-trichloro-*m*-cresol.

After two to three hours, tetrachloro-*m*-cresol.

After four hours and allowing the solution to remain in presence of the iron overnight, tetrachloro-*m*-cresol and a small quantity of 2 : 4 : 5-trichlorotoluquinone.

If the chlorination took place at the ordinary temperature, then, after three to four hours, there resulted pentachloromethyl*cyclo*hexadienone (XV).



(IX.) (XIII). (XV.) (XVI.)

Thus thymol, on chlorination in the presence of iron, even in an ice-cold solution, decomposed with the formation of trichloro-

*m*-cresol and *iso*propyl chloride. The trichloro-*m*-cresol was also obtained by the direct chlorination of *m*-cresol, and will be dealt with later. The *iso*propyl chloride could not be isolated satisfactorily, as it could not be separated from the large excess of carbon tetrachloride, in which solvent the chlorination was conducted. On distillation of the solution a fraction was obtained which seemed to be a mixture of *iso*propyl chloride and carbon tetrachloride of constant boiling point.

### 4. *Chlorination of Thymol in the Presence of Aluminium-Mercury.*

This catalyst has a very similar effect on the chlorination to that exerted by the reduced iron, but the action was not nearly so vigorous as in the case of the latter. The first product which could be isolated in this case was 2 : 4 : 6-trichloro-*m*-cresol.

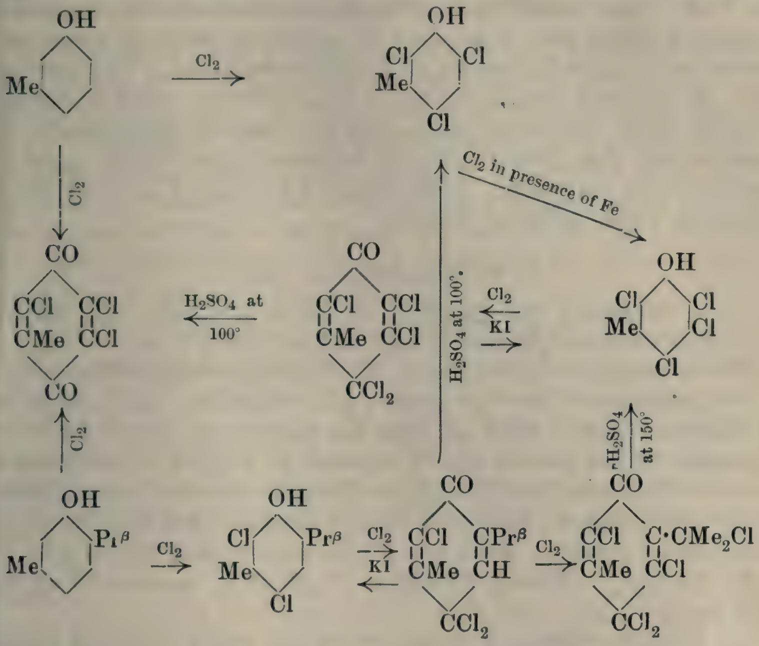
### 5. *Chlorination of* m-*Cresol.*

When chlorinated, *m*-cresol passes directly to the 2 : 4 : 6-trichloro-compound. The chlorination was carried out under different conditions, namely, (1) in the presence of reduced iron in ice-cold solution; (2) by leading chlorine for six hours into boiling *m*-cresol; and (3) in carbon tetrachloride solution at the ordinary temperature. All these three methods of chlorination gave, as first product, 2 : 4 : 6-trichloro-*m*-cresol. The first two methods gave very impure products, which required many recrystallisations before the substance was obtained in a pure state. After evaporating off the solvent, the third method was found to give by far the purest product.

A compound obtained by the direct chlorination of boiling *m*-cresol is described by Claus and Schweitzer (*Ber.*, 1886, **19**, 930) as dichloro-*m*-cresol. These experimenters give the melting point of their compound as 46°, which is identical with that of the trichloro-compound prepared by the authors. Many attempts have been made to prepare a mono- and a dichloro-*m*-cresol by chlorination for different periods of time in carbon tetrachloride solution. These all failed, for the first product which was invariably obtained was trichloro-*m*-cresol. The trichloro-*m*-cresol yields a methyl and an acetyl derivative, and, from analyses of these two compounds and also of the parent phenol, it seems evident that Claus and Schweitzer were mistaken.

Further chlorination of *m*-cresol in presence of a catalyst gave rise simply to the higher chlorination products which have been described earlier in dealing with the chlorination of thymol.

The following diagram shows the products which have been obtained, under different conditions, by the action of chlorine on thymol and on *m*-cresol.



### EXPERIMENTAL.

2 : 4 : 4 :-*Trichloro*-3-*methyl*-6-iso*propyl*-$\Delta^{2:5}$-cyclo*hexadienone*, $C_{10}H_{11}OCl_3$ (VIII).

This compound was prepared by the direct chlorination of thymol without any solvent or catalyst. Under the influence of the chlorine the solid thymol gradually liquefied with a considerable evolution of heat, the liquid became dark brown, and then, on continued chlorination, this colour disappeared. The chlorination was stopped when the weight had increased by about two-thirds. A mass of yellow crystals separated when the liquid was allowed to remain at the ordinary temperature for some hours; the crystals were collected and recrystallised from methyl alcohol, when the substance separated in bright yellow needles, which melted at 63°:

0·2022 gave 0·3418 AgCl. Cl = 41·81.

$C_{10}H_{11}OCl_3$ requires Cl = 42·01 per cent.

2 : 4 : 4 - *Trichloro*-3-*methyl*-6-iso*propyl* - $\Delta^{2:5}$-cyclo*hexadienone* is readily soluble in acetic acid, acetone, ether, chloroform, or light petroleum in the cold, and also in hot alcohol. It is insoluble in potassium or sodium hydroxides, but is decomposed by them slowly

on warming. The substance is also decomposed by concentrated sulphuric acid at 100°, with little or no charring, and the formation of 2 : 4 : 6-trichloro-*m*-cresol. The trichloro*cyclo*hexadienone readily liberates iodine from a solution of potassium iodide in acetic acid solution, with the formation of 2 : 6-dichlorothymol. This reaction can be followed quantitatively if the liberated iodine is titrated rapidly in an ice-cold solution with *N*/10-sodium thiosulphate. It was found that 0·3957 gram of substance gave 0·4080 gram of iodine; the equation $C_{10}H_{11}OCl_3 + 2KI = C_{10}H_{11}Cl_2OK + KCl + I_2$ requires 0·3965 gram of iodine.

### 2 : 6-*Dichlorothymol* (III).

This compound was prepared by Blum (*loc. cit.*) by heating 2 : 6-dichlorothymolglycuronic acid with sulphuric acid.

We obtained it by treating 2 : 4 : 4-trichloro-3-methyl-6-*iso*propyl-$\Delta^{2:5}$-*cyclo*hexadienone in acetic acid solution with excess of potassium iodide. After allowing the mixture to remain for a few minutes, it was poured into a solution of sodium thiosulphate to remove the iodine, and the yellow oil which separated was extracted with ether, washed, dried over sodium sulphate, and distilled under diminished pressure, when the 2 : 6-dichlorothymol passed over at 135°/12 mm. (Found, Cl = 32·7. $C_{10}H_{12}OCl_2$ requires Cl = 32·42 per cent.)

2 : 6-Dichlorothymol is a pale yellow oil, which is almost colourless when freshly distilled, but gradually darkens on exposure to air and light. It is soluble in most organic solvents and in sodium or potassium hydroxides. It does not liberate iodine from potassium iodide. When 2 : 6-dichlorothymol was subjected to direct chlorination, hydrogen chloride was evolved, and 2 : 4 : 4-trichloro-3-methyl-6-*iso*propyl-$\Delta^{2:5}$-*cyclo*hexadienone resulted.

2 : 6-*Dichlorothymol Methyl Ether*, $C_{10}H_{11}Cl_2 \cdot OMe$.—This derivative was prepared by warming 2 : 6-dichlorothymol with excess of methyl sulphate, destroying the excess of the latter with sodium carbonate, and pouring the resulting solution into water. The oil which separated was extracted with ether, and washed with dilute potassium hydroxide to remove traces of the unchanged phenol, and then with water. The solution was dried over sodium sulphate, and distilled under diminished pressure, when it passed over at 129°/12 mm.:

0·1871 gave 0·2316 AgCl. Cl = 30·55.

$C_{11}H_{14}OCl_2$ requires Cl = 30·47 per cent.

This methyl derivative is a yellow oil very similar in appearance to 2 : 6-dichlorothymol. It is soluble in most organic solvents, but is insoluble in sodium hydroxide.

### 2:4:4:5-*Tetrachloro*-3-*methyl*-6-β-*chloro*iso*propyl*-$\Delta^{2:5}$-cyclo-*hexadienone*, $C_{10}H_9OCl_5$ (XIV).

This compound could be prepared only in small quantities by the chlorination, for several hours at the ordinary temperature, of thymol in the presence of iodine, in dilute carbon tetrachloride or acetic acid solutions. The solvent was removed by evaporation, and from the residue, after it had remained for several days, there separated out a few crystals of the *cyclo*hexadienone. The product was crystallised from light petroleum, methyl alcohol, or acetic acid, when it separated in white, flat needles, which melted at 95°:

0·1598 gave 0·3548 AgCl. Cl = 54·93.

$C_{10}H_9OCl_5$ requires Cl = 55·04 per cent.

This compound formed no acetyl or benzoyl derivatives, and was insoluble in sodium or potassium hydroxides, being slowly decomposed by them on warming. On heating the substance in alcoholic solution it liberated iodine from potassium iodide. The compound was decomposed with much charring by concentrated sulphuric acid at 150°, with the formation of tetrachloro-*m*-cresol, which separated as a solid from the hot acid.

### 2:4:6-*Trichloro*-m-*cresol*, $C_7H_5OCl_3$ (IX).

This substance was prepared by the chlorination, in the presence of iron for about one to two hours, of 3—4 grams of thymol in carbon tetrachloride solution. The solution was cooled in ice, and after evaporating off the solvent a white mass was obtained, which required to be recrystallised five or six times from dilute acetic acid or light petroleum before it was obtained pure. It can also be prepared by the chlorination for several hours of boiling *m*-cresol, and also by the chlorination of *m*-cresol in carbon tetrachloride solution. This last method yields by far the best product. Another method for its preparation is the action of concentrated sulphuric acid at 100° on 2:4:4-trichloro-3-methyl-6-*iso*propyl-$\Delta^{2:5}$-*cyclo*hexadienone. The substance, after several recrystallisations, melted at 46°:

0·1924 gave 0·3921 AgCl. Cl = 50·42.

$C_7H_5OCl_3$ requires Cl = 50·35 per cent.

2:4:6-*Trichloro*-m-*cresol* is extremely soluble in all the ordinary organic solvents except light petroleum, it is sparingly soluble in boiling water, and readily so in sodium or potassium hydroxides. It has no action on potassium iodide, has a very penetrating odour, and is easily volatile in steam.

2:4:6-*Trichloro*-m-*tolyl Methyl Ether*, $C_7H_4Cl_3{\cdot}OMe$.—This compound was prepared by warming trichloro-*m*-cresol with excess of methyl sulphate. The excess of the latter was removed with sodium carbonate, and the solid methyl derivative was separated and crystallised from dilute acetic acid, when it separated in small, slender, white needles, which melted at 54—55°:

0·1974 gave 0·3792 AgCl. Cl=47·52.

$C_8H_7OCl_3$ requires Cl=47·23 per cent.

*Acetyl Derivative*, $C_7H_4Cl_3\cdot OAc$.—This derivative was prepared by the action of acetic anhydride on trichloro-*m*-cresol in the presence of a drop of concentrated sulphuric acid. The mixture was poured into water, and the oil which separated was extracted with ether, washed with dilute potassium hydroxide and with water, and allowed to solidify in a vacuum desiccator. The crystals were separated and purified by a second extraction with ether, when they melted at 32°:

0·2031 gave 0·3435 AgCl. Cl=41·84.

$C_9H_7O_2Cl_3$ requires Cl=42·01 per cent.

### 2:4:5:6-*Tetrachloro*-m-*cresol*, $C_7H_4OCl_4$ (XIII).

This compound was obtained by the more or less prolonged chlorination of thymol in presence of iodine in a concentrated carbon tetrachloride solution. If iron were used as the catalyst, 3 grams of thymol were converted into tetrachloro-*m*-cresol after chlorination for two to three hours even in an ice-cold solution. The tetrachlorocresol separated out from a concentrated solution as a crystalline mass, and, at this point, the chlorination was arrested as the tetrachlorocresol was very easily chlorinated further.

The best method, however, for the preparation of tetrachloro-*m*-cresol consists in treating 2:4:4:5:6-pentachloro-3-methyl-$\Delta^{2:5}$-*cyclo*hexadienone (the final product of the chlorination of thymol or of *m*-cresol) with excess of potassium iodide, the reaction being carried out in alcoholic or acetic acid solutions. The mixture is poured into sodium thiosulphate solution, and the yield is practically theoretical.

As described previously, tetrachloro-*m*-cresol is also formed by treating 2:4:4:5-tetrachloro-3-methyl-6-β-chloro*iso*propyl-$\Delta^{2:5}$-*cyclo*hexadienone with sulphuric acid at 150°.

When crystallised from light petroleum, acetic acid, or dilute alcohol, tetrachloro-*m*-cresol separates in slender, white, long needles, which melt at 189—190°:

0·1732 gave 0·4048 AgCl. Cl=57·84.

$C_7H_4OCl_4$ requires Cl=57·73 per cent.

2:4:5:6-*Tetrachloro*-m-*cresol* is soluble in most organic solvents, and dissolves in potassium hydroxide, but is unattacked by warm concentrated sulphuric acid. It can be converted easily into acetyl and benzoyl derivatives, and, when treated with chlorine in carbon tetrachloride solution, it yields 2:4:4:5:6-pentachloro-3-methyl-$\Delta^{2:5}$-*cyclo*hexadienone.

*Acetyl Derivative,* $C_7H_3Cl_4\cdot OAc$.—This compound was prepared by the action of acetic anhydride on tetrachloro-*m*-cresol in the presence of a drop of sulphuric acid. On crystallisation from glacial acetic acid it separated in flat needles, which melted at 117°:

0·1955 gave 0·3877 AgCl. Cl=49·07.

$C_9H_6O_2Cl_4$ requires Cl=49·30 per cent.

This compound is insoluble in cold alcohol, but is soluble in cold acetone or ether. It is readily hydrolysed by alcoholic potassium hydroxide.

*Benzoyl Derivative,* $C_7H_3Cl_4\cdot OBz$.—This derivative was prepared in pyridine solution, and, when crystallised from glacial acetic acid or alcohol, melted at 143—144°:

0·1998 gave 0·3278 AgCl. Cl=40·59.

$C_{14}H_8O_2Cl_4$ requires Cl=40·57 per cent.

### 2:4:4:5:6-*Pentachloro*-3-*methyl*-$\Delta^{2:5}$-cyclo*hexadienone*, $C_7H_3OCl_5$ (XV).

This compound was found to be the chief and final product of the complete chlorination of thymol in presence of either iodine or iron. The thymol was dissolved in a small quantity of carbon tetrachloride, a little iron or iodine was added, and a stream of dry chlorine was passed through the solution until the evolution of hydrogen chloride had ceased. In the case of iodine as the catalyst, 5 grams of thymol required chlorination during two days at 60° before the process was complete. With iron, however, the same quantity of thymol required only about four to five hours' chlorination at the ordinary temperature. The pentachlorohexadienone, when crystallised from light petroleum, glacial acetic acid, or alcohol, separated in large, rhombic prisms with a slight yellowish-green tinge, which melted at 92°:

0·1386 gave 0·3528 AgCl. Cl=62·96.

$C_7H_3OCl_5$ requires Cl=63·28 per cent.

2:4:4:5:6-*Pentachloro*-3-*methyl*-$\Delta^{2:5}$-cyclo*hexadienone* is readily soluble in acetone, benzene, toluene, chloroform, or ether in the cold, but it is insoluble in water. No acetyl or benzoyl derivatives of it could be obtained, and it is insoluble in alkalis. It liberates iodine from potassium iodide in alcoholic or acetic acid solutions, and this reaction was followed quantitatively with the following result: 0·4650 gram of substance yielded 0·4215 gram of iodine. The equation $C_7H_3OCl_5 + 2KI = C_7H_3Cl_4OK + KCl + I_2$ requires 0·4210 gram of iodine.

Concentrated sulphuric acid at 100° oxidises the compound very readily to 2:4:5-trichlorotoluquinone, which separates from the hot acid as a yellow, crystalline mass.

### 2:4:5-*Trichlorotoluquinone*, $C_7H_3O_2Cl_3$ (XVI).

This compound was obtained in small quantities, together with tetrachloro-*m*-cresol and 2:4:4:5:6-pentachloro-3-methyl-$\Delta^{2:5}$-*cyclo*hexadienone, by the prolonged chlorination of thymol in the presence of iodine or reduced iron. In the presence of iodine the chlorination required about ten days, but with reduced iron small quantities of the toluquinone were obtained after chlorination for twelve hours.

The best method of preparation consists in treating 2:4:4:5:6-pentachloro-3-methyl-$\Delta^{2:5}$-*cyclo*hexadienone with concentrated sulphuric acid at 100°. After a few minutes a yellow, crystalline mass separates, and the reaction is found to be practically quantitative. The substance was recrystallised from a mixture of alcohol and benzene, and melted and decomposed at 238°:

0·1769 gave 0·3368 AgCl. Cl = 47·10.

$C_7H_3O_2Cl_3$ requires Cl = 47·23 per cent.

The identity of this substance was established by a mixed melting-point determination with a specimen of trichlorotoluquinone prepared by the oxidation of *o*-toluidine with sodium dichromate.

CHEMICAL DEPARTMENT,
THE UNIVERSITY, EDGBASTON.
BIRMINGHAM.

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## LXII.—*The Constituents of the Oil of* Cydnus indicus.

By EDWIN ROY WATSON.

*Cydnus indicus* (Westw.) is an insect which is well known in many parts of India. In Bengal it is attracted to lights, often in large numbers, in the nights of June and the following rainy months. It is notorious on account of its strong and unpleasant odour, which is so strong that one insect is sufficient to scent a whole room. In the vernacular it is known as *gandi*. It is also known as the *geranium-bug*. The last name perhaps indicates a supposed similarity of the odour to that of the geranium.

The insect is one of the Heteroptera. Maxwell-Lefroy (*Indian Insect Life*) remarks that "a feature of the great majority of the Heteroptera is the aromatic odour they protect themselves with. This odour is due to the secretion by special glands of an oily fluid, which is excreted at will from the odoriferous orifices and rapidly volatilises."

The insects used for this investigation * were collected in Dacca (E. Bengal) in June. Altogether 453 grams [1 lb.] of material were collected, and estimated to consist of 100,000 insects. They contain a large quantity of oil, and this, after extraction, was found to possess the characteristic and disagreeable odour. A preliminary examination showed that it was mainly a fixed oil of the same general character as other animal oils. It was then found that if the insects were crushed and distilled in a current of steam a small quantity of an oily substance passed over and collected as a lighter layer above the condensed water, and had the characteristic odour, highly concentrated. Ultimately the best yield was obtained by extracting the insects with ether, distilling off the ether on the water-bath, and subjecting the oil to steam distillation. It was thus separated into two parts, namely, (*A*) a volatile oil, and (*B*) a non-volatile oil.

The volatile portion was redistilled with steam for further purification. One hundred grams of the insects gave about 1·5 grams of redistilled volatile oil and about 70 grams of the non-volatile oil.

(A) *The Volatile Oil*.—This was separated from the steam distillate by shaking with ether. The ethereal solution was dried, and the ether allowed to evaporate at the ordinary temperature over soda-lime:

0·1193 gave 0·1111 $H_2O$ and 0·3021 $CO_2$. C = 69·07; H = 10·34.

$C_9H_{16}O_2$ requires C = 69·2; H = 10·3 per cent.

This result was not in accordance with the anticipation that this strongly-smelling oil would prove to be a terpene or terpene-alcohol, aldehyde, or ketone. From the high percentage of oxygen it seemed probable that it was a carboxylic acid, or contained a good deal of such an acid substance; and this conjecture was borne out by experiment, for on shaking the oil with dilute aqueous sodium carbonate the greater part of it (about 90 per cent.) passed into solution. The undissolved non-acidic portion was recovered by extraction with ether, drying, and freeing from ether as before.

The alkaline solution was acidified with dilute sulphuric acid, when the acid portion of the oil was liberated. It was likewise extracted with ether, dried, and freed from ether.

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* A sample was identified by Dr. N. Annandale of the Indian Museum, not as *Cydnus indicus*, but as the closely-related species *Stibaropus molginus*, *Schiodte*.

*The Acidic Portion of the Volatile Oil.*—Examination showed this to consist of a single substance of the empirical formula $C_8H_{14}O_2$, probably *cyclo*heptanecarboxylic acid. (Found, C = 67·49; H = 10·12; M.W. (by titration with alkali), 141. Calc., C = 67·60; H = 9·86 per cent.; M.W. = 142.)

The exactly neutral solution obtained by the titration of the acid was treated with a solution of calcium chloride and, on keeping, gave a deposit of uniform prismatic crystals of a calcium salt. Further crops of the same crystalline character were obtained by concentrating the solution and allowing to cool. Care was necessary not to carry the concentration too far, or else the calcium salt was deposited from the hot solution, first as a skin on the surface, and then as a semi-solid mass, which solidified on cooling. (Found, $H_2O = 5{\cdot}1$. $(C_8H_{13}O_2)_2Ca,H_2O$ requires $H_2O = 5{\cdot}3$ per cent. Found,* C = 58·05 †; H = 8·22; CaO = 17·61. $(C_8H_{13}O_2)_2Ca$ requires C = 59·64; H = 8·08; CaO = 17·39 per cent.)

The exact agreement of the analytical figures for the oil with the formula $C_8H_{14}O_2$, that of the acid corresponding with the calcium salt which was obtained in pure condition, shows that the oil is a single substance. It boils at 251°, has a strongly acid reaction towards litmus, and shows no tendency to absorb halogen. The acid has a strong, rancid odour, and thus appears to be *cyclo*-heptanecarboxylic acid.

*Non-acidic Portion of the Volatile Oil.*—The quantity of this substance obtained was only sufficient for ultimate analysis:

0·0970 gave 0·2552 $CO_2$ and 0·0932 $H_2O$. C = 71·74; H = 10·68.

$C_{11}H_{20}O_2$ requires C = 71·73; H = 10·86 per cent.

It would not be safe to draw any conclusions as to the constitution of the substance from this analysis alone. It may, however, be remarked that the figures are opposed to the idea that the substance is a terpene, terpene-alcohol, aldehyde, or ketone. This portion of the oil had an odour quite different from that of the acid. To the author it resembled the odour of lemon or geranium, but to others this resemblance was not obvious, and by them it was thought to have the original odour of the insects in a highly concentrated form.

(B) *The Non-volatile Oil.*—The analytical figures obtained show this to be very similar to other animal oils, and as it does not contribute appreciably to the odour of the insect it possesses no special interest.

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* In salt dried at 140°.

† The Ca salt was mixed with potassium dichromate in the combustion boat, but this does not appear to have been sufficient to effect the liberation of the whole of the carbon.

| | |
|---|---|
| $D_{15\cdot5^\circ}^{15\cdot5^\circ}$ | 0·9135 |
| Free acid (calculated as stearic acid) | 6·6 per cent. |
| Insoluble fatty acids (obtained on saponification) | 94·8 ,, ,, |
| Volatile fatty acids (reckoned as butyric acid) | 0·6 ,, ,, |
| Potassium hydroxide required for saponification | 19·1 ,, ,, |
| Iodine absorption | 49·1 ,, ,, |

This examination showed that the non-volatile oil did not contain the glyceride of *cyclo*heptanecarboxylic acid.

## *Conclusion.*

The strong and disagreeable odour of *Cydnus indicus* is due to *cyclo*heptanecarboxylic acid which is present in the insects to the amount of 1½ per cent., and another substance ($C_{11}H_{20}O_2$?) or mixture of substances, present in much smaller quantity (0·1—0·2 per cent.), which has a still stronger odour. The intensity of the odour of the latter substance can be judged from the fact that each insect contains only 0·000005 gram of it, and yet one insect is sufficient to scent a whole room.

More material will be obtained in June, 1913, and the investigation of this substance continued.

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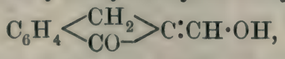
# LXIII.—*Studies on Cyclic Ketones. Part III.*

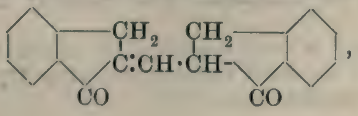
By Siegfried Ruhemann and Stanley Isaac Levy.

In Part II. of the present work (T., 1912, **101**, 2542) it was shown that the behaviour of 2-hydroxymethylene-1-hydrindene,

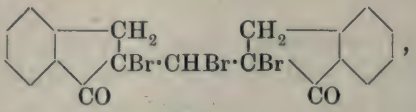


$$C_6H_4{<}\begin{matrix}CH_2\\CO\end{matrix}{>}C{:}CH{\cdot}OH,$$

and its methylenedioxy-derivative differs from that of hydroxymethylenecamphor and other hydroxymethylene compounds, inasmuch as the former are not stable towards heat; thus at the melting point they condense, with the loss of one molecule of formic acid from two molecules of the hydroxymethylene derivative, to the coloured ketohydrindylmethyleneketohydrindene,

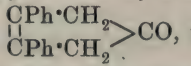


and the corresponding methylenedioxy-derivative respectively. The constitution of these substances, which, as previously stated (*loc. cit.*), follows from the syntheses and from the formation of salts with alkalis, is supported by their behaviour towards bromine. The condensation product from hydroxymethylenehydrindone yields the colourless tribromo-compound, $C_{19}H_{13}O_2Br_3$. Besides the addition of bromine at the ethylene linking, therefore, it follows that substitution of one hydrogen atom by the halogen also occurs. The fact that the total halogen is readily removed by potassium hydroxide points to the formula:



(I.)

for the bromo-compound.

The remarkable transformation which these hydroxymethylene compounds undergo on heating induced us to prepare analogous derivatives from other cyclic ketones. Having found (*loc. cit.*) that neither 1 : 3-dimethyl-6-hydroxymethylene-$\Delta^3$-*cyclo*hexen-5-one nor 3-methyl-5-hydroxymethylene*cyclo*pentan-1-one * undergoes any change on heating, we endeavoured to prepare the hydroxymethylene derivative of 2-hydrindone, in the hope that it would behave similarly to the corresponding derivative of 1-hydrindone. It was found, however, that this compound cannot be obtained by the usual method, the hydrindone being transformed into a viscous product. Various attempts to prepare the hydroxymethylene derivative of diphenyl*cyclo*pentenone,  $\begin{matrix}\text{CPh}\cdot\text{CH}_2\\ \|\\ \text{CPh}\cdot\text{CH}_2\end{matrix}\!\!>\text{CO}$, were equally unsuccessful; we could obtain only a very small quantity of a yellow substance, which, although giving in alcoholic solution a strong coloration with ferric chloride, was found to be a mixture.

This unexpected result induced us to subject this cyclic ketone to a closer study, with the view of ascertaining whether it condenses with ethyl oxalate and aromatic aldehydes, and whether the action occurs between one molecule of the ketone and two molecules of these reagents. The investigation appeared to us of interest, also, for another reason. Some time ago (Ruhemann and Naunton, T., 1912, **101**, 42) it was shown that the azomethines which are produced by the action of *p*-nitrosodimethylaniline on diphenyl*cyclo*pentenone, yield, on treatment with mineral acids, 5-*p*-dimethylaminoanilo-3 : 4-diphenyl-$\Delta^{3:4}$-*cyclo*pentene-1 : 2-dione,

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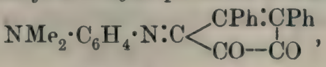
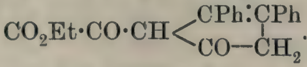
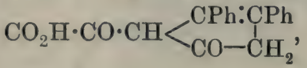
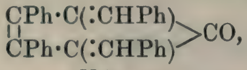
* The authors regret to have overlooked the fact that 3-methyl-5-hydroxymethylene*cyclo*pentan-1-one, which they described in Part II, was obtained before by Wallach (*Annalen*, 1903, **329**, 109).


$$\mathrm{NMe_2\cdot C_6H_4\cdot N\colon C}<\begin{matrix}\mathrm{CPh\colon CPh}\\ \mathrm{CO{-}{-}CO}\end{matrix},$$

which is characterised by the ease with which its solutions are transformed into the colloidal state (see also Hardy, *Proc. Roy. Soc.*, 1912, *A*, **87**, 29); and it was in the hope that the further study of diphenyl*cyclo*pentenone might bring to light other derivatives of the ketone which possess properties similar to those of the azomethine, that we undertook this work.

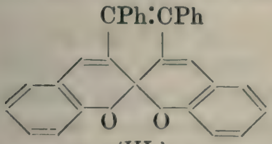
It was to be expected that the cyclic ketone would condense with ethyl oxalate to form ethyl diphenyl*cyclo*pentenonedioxalate, but this compound could not be obtained, only one molecule of the ester taking part in the reaction to yield *ethyl* 3 : 4-*diphenyl*-$\Delta^{3:4}$-cyclo-*pentenone*-2-*oxalate*,  $\mathrm{CO_2Et\cdot CO\cdot CH}<\begin{matrix}\mathrm{CPh\colon CPh}\\ \mathrm{CO{-}CH_2}\end{matrix}$. The yield is unsatisfactory, the larger part of the ketone remaining unaltered. The ester decomposes readily when warmed with dilute potassium hydroxide to the original ketone and potassium oxalate, although if the reaction mixture is allowed to remain for a day without heating, the *acid*,  $\mathrm{CO_2H\cdot CO\cdot CH}<\begin{matrix}\mathrm{CPh\colon CPh}\\ \mathrm{CO{-}CH_2}\end{matrix}$, is obtained on the addition of dilute mineral acids.

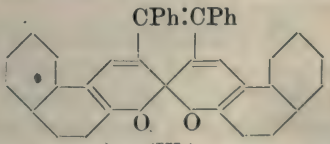
On the other hand, diphenyl*cyclo*pentenone readily condenses with two molecules of aromatic aldehydes when the solution of the mixture in alcohol or glacial acetic acid is saturated with hydrogen chloride. With benzaldehyde, 3 : 4-*diphenyl*-2 : 5-*dibenzylidene*-$\Delta^{3:4}$-cyclo*pentenone*,


$$\begin{matrix}\mathrm{CPh\cdot C(\colon CHPh)}\\ \Vert\\ \mathrm{CPh\cdot C(\colon CHPh)}\end{matrix}>\mathrm{CO},$$

(II.)

is formed; similar compounds have been obtained by the action of *p*-nitrobenzaldehyde and of cinnamaldehyde on the ketone. The behaviour of salicylaldehyde is of special interest; as in the above cases, the ketone condenses with two molecules of the aldehyde, but the disalicylidene derivative which is undoubtedly first formed loses a further molecule of water, yielding the yellow pentacyclic anhydride, 3 : 3′-*diphenylacetylenedibenzo*spiro*pyran* (III). Similar compounds have recently been obtained by Borsche and Geyer

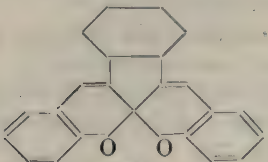

(III.)


(IV.)

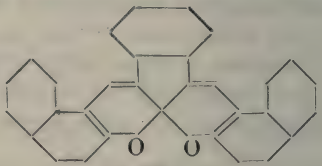
(*Annalen*, 1912, **393**, 29) from saturated alicyclic ketones; we adopt here the system of nomenclature which these authors have given.

In the same way, 2-naphthol-1-aldehyde reacts with diphenyl*cyclo*pentenone, forming the yellowish-brown heptacyclic compound, *diphenylacetylenedi-β-naphtha*spiro*pyran* (IV).

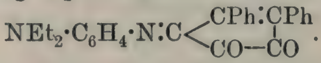
As was to be expected, 2-hydrindone reacts with salicylaldehyde as well as with 2-naphthol-1-aldehyde, to yield the hexa- and octacyclic *spiro*pyran compounds, *phenylenedibenzo*spiro*pyran* (V) and *phenylenedi-β-naphtha*spiro*pyran* (VI), which are red and bluish-black respectively. These cyclic compounds, with the exception of (VI), are characterised by the deep green fluorescence of their solutions in cold concentrated sulphuric acid; in the case of the latter substance, the fluorescence develops only after boiling, and in no case is it apparent in solutions of these substances in other solvents.



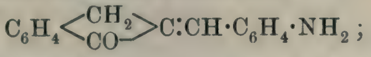
(V.)



(VI.)

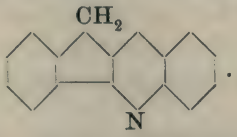
None of the above-mentioned condensation products of diphenyl*cyclo*pentenone has the property of the azomethine, $C_{25}H_{20}O_2N_2$, of being transformed in solution into the colloidal state. This result induced us to examine whether this phenomenon occurs in the case of the corresponding 5-p-*diethylaminoanilo*-3:4-*diphenyl*-$\Delta^{3:4}$-cyclo*pentene*-1:2-*dione*,  $\mathrm{NEt_2\cdot C_6H_4\cdot N{:}C}<\begin{array}{l}\mathrm{CPh{:}CPh}\\ \mathrm{CO{-}CO}\end{array}$. This substance is obtained by a method similar to that employed in the case of the dimethyl derivative, namely, by treating the product of the action of *p*-nitrosodiethylaniline on diphenyl*cyclo*pentenone with hydrochloric acid. We were surprised to find that the solutions of this compound do not pass into the colloidal state; it seems, therefore, that this behaviour is peculiar to the particular azomethine, $C_{25}H_{20}O_2N_2$, since, as previously stated (*loc. cit.*), it is not observed either with the bromo- or nitro-substitution products of this compound.

Since aromatic *o*-hydroxy-aldehydes condense with diphenyl*cyclo*pentenone and 2-hydrindone to form *spiro*pyran compounds, it occurred to us that aromatic *o*-amino-aldehydes might react with these ketones in a similar manner, to yield *spiro*-compounds containing nitrogen. We are at present engaged in the study of this reaction. In the meantime, we have investigated the behaviour of *o*-aminobenzaldehyde towards 1-hydrindone, and find that, under the influence of potassium hydroxide, condensation occurs to the orange 2-*o*-aminobenzylidene-1-hydrindone,



$$C_6H_4{<}{\overset{CH_2}{\underset{CO}{}}}{>}C{:}CH{\cdot}C_6H_4{\cdot}NH_2\,;$$

under the conditions of the reaction, this substance partly condenses, with loss of one molecule of water, to the colourless indenoquinoline,



The change is complete on boiling the aminobenzylidenehydrindone with hydrochloric acid, when the unstable hydrochloride of the quinoline is formed; this dissociates, on boiling with water, into hydrochloric acid and the free base.

Indenoquinoline has been described by Noelting and Blum (*Ber.*, 1901, **34**, 2467), who obtained it from ketoindenoquinoline, the product of the interaction of *o*-aminobenzaldehyde and 1 : 3-diketohydrindene, by distillation with zinc dust. These authors give the names quinolylenephenylenemethane and quinolylene phenylene ketone respectively to these compounds, but it appears to us to be more convenient to use the above names, which correspond with the nomenclature generally adopted for polycyclic systems.

## EXPERIMENTAL.

### *Action of Bromine on Ketohydrindylmethyleneketohydrindene.*

This reaction takes place on gradually adding bromine to the red condensation product of 2-hydroxymethylene-1-hydrindone, suspended in glacial acetic acid. The halogen is absorbed, and at the same time the solid dissolves, forming a red solution. The clear liquid is kept overnight, and then treated with water, which precipitates a white solid, very sparingly soluble in light petroleum and alcohol, but dissolving readily in boiling benzene. The hot benzene solution is treated with light petroleum (b. p. 60—70°) until it becomes turbid; on cooling, the solid separates in colourless needles, which melt and decompose at 156°:

0·1903 gave 0·3095 $CO_2$ and 0·0511 $H_2O$. C=44·36; H=2·98.
0·2580 „ 0·2822 AgBr. Br=46·53.
$C_{19}H_{13}O_2Br_3$ requires C=44·44; H=2·53; Br=46·78 per cent.

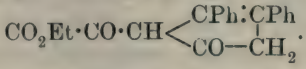
The *dibromide* of *ketohydrindylmethyleneketobromohydrindene* (I) readily loses its whole content of bromine on the addition of alcoholic potassium hydroxide to the hot alcoholic solution. The mixture develops a deep red coloration, which at first rapidly disappears, remaining permanent only when a slight excess over the required amount (3 molecules) of the alkali has been added. On concentration, the solution deposits a faintly yellow solid, which is insoluble in water, but dissolves, although not readily, in potassium hydroxide to yield a red solution. Qualitative tests show that it contains no bromine, but as yet the nature of the compound has not been further studied.

### *Action of Ethyl Formate on* 3:4-*Diphenyl*cyclo*pentenone.*

The *cyclo*pentenone required for this work was prepared, as previously (T., 1912, **101**, 42), according to the directions of Japp and Lander (T., 1897, **71**, 131). It was found, however, that the yield of the pure compound is considerably greater than, indeed, more than twice as great as that given by these authors. With the object of preparing the hydroxymethylene derivative of the *cyclo*pentenone and studying its behaviour, the ketone (4·6 grams) was dissolved in absolute ether (of which a large volume is required, owing to the sparing solubility in this solvent), and mixed with ethyl formate (3·1 grams, two molecules); on gradually adding the solution to sodium ethoxide (2·7 grams, two molecules) suspended in ether, the whole being maintained at 0°, a deep red coloration was immediately developed, and a small quantity of a dark solid separated, which, however, did not perceptibly increase on keeping. After three days the whole was shaken with ice-water, and the aqueous layer, after being freed from ether by means of a current of air, was acidified with acetic acid. A very small quantity of a yellow solid was precipitated, but although the alcoholic solution gave a green coloration with ferric chloride, the product proved to be a mixture from which no pure substance could be separated.

An attempt to carry out the condensation, using quantities corresponding with one molecule each of ketone, ester, and sodium ethoxide, was even less successful; on acidifying the aqueous layer obtained from the reaction mixture only a slight opalescence was observed. Finally, the ketone was heated with excess of ethyl formate to 150° in a sealed tube for an hour, in the hope that the hydroxymethylene derivative which might be formed would condense to a coloured compound analogous to that obtained from 2-hydroxymethylene-1-hydrindone; on opening the tube, however, the reagents were found to have remained unchanged.

### *Ethyl* 3:4-*Diphenyl*-$\Delta^{3:4}$-cyclo*pentenone-2-oxalate*,



$$CO_2Et\cdot CO\cdot CH<\begin{matrix}CPh:CPh\\ |\\ CO-CH_2\end{matrix}.$$

This ester is formed, in place of the ethyl diphenyl*cyclo*pentenonedioxalate, which might have been expected, when the *cyclo*pentenone is treated with two equivalents of sodium ethoxide and ethyl oxalate. On adding the mixture of the ketone (4·7 grams) and ethyl oxalate (6·0 grams), dissolved in absolute ether, to sodium ethoxide (2·8 grams) suspended in ether, the liquid darkens, and deposits a brown solid, which gradually increases in quantity. After keeping for four days, the solid is collected and treated with dilute sulphuric acid, and the whole extracted with ether. The yellow substance left on evaporation of the ethereal solution, is readily soluble in hot dilute alcohol, from which it crystallises on cooling in light yellow needles melting at 131—132°. The alcoholic solution gives a reddish-brown coloration with ferric chloride:

0·2039 gave 0·5652 $CO_2$ and 0·0985 $H_2O$. C = 75·60; H = 5·36.

$C_{21}H_{18}O_4$ requires C = 75·45; H = 5·39 per cent.

*Ethyl* 3:4-*diphenyl*-$\Delta^{3:4}$-cyclo*pentenone*-2-*oxalate* readily dissolves in dilute potassium hydroxide; on heating for a short time, the solution deposits a solid which was identified with the *cyclo*pentenone, and the alkaline liquid then contains oxalic acid. Under these conditions, therefore, the ester decomposes. Hydrolysis to the acid, however, can be effected by the action of dilute potassium hydroxide at the ordinary temperature. On keeping the alkaline solution overnight, and then adding dilute hydrochloric acid, 3:4-*diphenyl*-$\Delta^{3:4}$-cyclo*pentenone*-2-*oxalic acid* separates as a deep yellow solid, which crystallises from hot dilute alcohol in long needles; the alcoholic solution gives a reddish-brown coloration with ferric chloride. The substance melts gradually at 175—183°, this behaviour being probably due to the presence of a small quantity of unchanged ester:

0·2076 gave 0·5675 $CO_2$ and 0·0923 $H_2O$. C = 74·55; H = 4·94.

$C_{19}H_{14}O_4$ requires C = 74·51; H = 4·58 per cent.

### *Action of Aromatic Aldehydes on Diphenyl*cyclo*pentenone.*

### 3:4-*Diphenyl*-2:5-*dibenzylidene*-$\Delta^{3:4}$-cyclo*pentenone* (II).

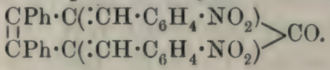
Benzaldehyde does not condense with the *cyclo*pentenone under the influence of heat, even when the mixture is kept at 180°. An action occurs, however, on adding alcoholic potassium hydroxide to the mixture of aldehyde and ketone, dissolved in alcohol, at the ordinary temperature, but the quantity of solid which separates is quite inconsiderable, even after several days. The condensation takes place much more readily when hydrogen chloride is used, instead of the alkali. The solution of the ketone (3 grams) and the aldehyde (2·7 grams) in glacial acetic acid, after saturation with the gas at 0°, develops a deep red coloration, and in the course of three days the whole sets to a semi-solid mass of red crystals. The product is almost insoluble in cold alcohol, but dissolves sparingly in the boiling solvent; on cooling, it crystallises in orange needles, which turn red and soften at about 190°, and melt at 201—202°:

0·2080 gave 0·6915 $CO_2$ and 0·1005 $H_2O$. $C=90·67$; $H=5·37$.

$C_{31}H_{22}O$ requires $C=90·73$; $H=5·37$ per cent.

The substance dissolves gradually in cold concentrated sulphuric acid, forming a yellowish-brown solution, which gradually deepens in colour.

3 : 4-*Diphenyl*-2 : 5-*di*-p-*nitrobenzylidene*-$\Delta^{3:4}$-cyclo*pentenone*,



$$\left.\begin{array}{l}\mathrm{CPh{\cdot}C({:}CH{\cdot}C_6H_4{\cdot}NO_2)}\\ \|\\ \mathrm{CPh{\cdot}C({:}CH{\cdot}C_6H_4{\cdot}NO_2)}\end{array}\right\rangle\mathrm{CO}.$$

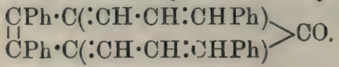
*p*-Nitrobenzaldehyde condenses with the *cyclo*pentenone when the solution of the two compounds in alcohol or glacial acetic acid is saturated with hydrogen chloride at 0°; the reaction is complete after keeping the mixture for a week. The red solid which separates is insoluble in alcohol, and only sparingly soluble in boiling glacial acetic acid. After washing with hot alcohol and drying in the steam-oven it melts and decomposes at about 308°:

0·1982 gave 0·5415 $CO_2$ and 0·0728 $H_2O$. $C=74·51$; $H=4·08$.
0·2375 „ 12·0 c.c. $N_2$ at 20° and 746 mm. $N=5·67$.

$C_{31}H_{20}O_5N_2$ requires $C=74·40$; $H=4·00$; $N=5·60$ per cent.

With cold concentrated sulphuric acid the compound dissolves to a brownish-green solution, which darkens considerably in colour after a short time.

3 : 4-*Diphenyl*-2 : 5-*dicinnamylidene*-$\Delta^{3:4}$-cyclo*pentenone*,



$$\left.\begin{array}{l}\mathrm{CPh{\cdot}C({:}CH{\cdot}CH{:}CHPh)}\\ \|\\ \mathrm{CPh{\cdot}C({:}CH{\cdot}CH{:}CHPh)}\end{array}\right\rangle\mathrm{CO}.$$

This compound, like the above, is readily obtained by the use of hydrogen chloride as a condensing agent. On passing the gas into the cooled mixture of the aldehyde (3·4 grams) and the ketone (3 grams) dissolved in glacial acetic acid, a deep red coloration develops, and after a day, the whole sets to a semi-solid mass of crystals. The product is insoluble in cold, sparingly soluble in hot, alcohol; it dissolves in much boiling glacial acetic acid, separating on cooling in scarlet needles, which soften at about 225° and melt at 234°:

0·2124 gave 0·7080 $CO_2$ and 0·1082 $H_2O$. C=90·90; H=5·66.
$C_{35}H_{26}O$ requires C=90·91; H=5·63 per cent.

The substance dissolves in cold concentrated sulphuric acid to a deep blue solution, which after a short time becomes reddish-violet, and finally red.

When alcoholic potassium hydroxide is employed in place of hydrogen chloride as a condensing agent, a viscous product is obtained; in the course of a day, this sets to a brittle, red solid, from which no crystalline substance could be isolated.

### *The Anhydride of* 3:4-*Diphenyl*-2:5-*disalicylidene*-$\Delta^{3:4}$-cyclo*pentenone* (3:3′-*Diphenylacetylenedibenzo*spiro*pyran*), (III).

On saturating the alcoholic solution of the *cyclo*pentenone (3 grams) and salicylaldehyde (3·2 grams) with hydrogen chloride at 0°, a dark red coloration develops; on keeping the mixture overnight, a yellow solid separates, which increases in quantity in the course of two days. The compound is almost insoluble in alcohol or glacial acetic acid, but dissolves sparingly in boiling nitrobenzene, from which it crystallises on cooling in yellow plates, which do not melt on heating to 320°; it is insoluble in potassium hydroxide, even on boiling. The crystals have the remarkable property of fixing the solvent to such an extent that prolonged washing with boiling alcohol does not entirely remove the nitrobenzene. On account of this fact, the analytical results differed appreciably, especially in the values obtained for carbon, from the theoretical values, and it was not until the compound had been heated in a vacuum at 160—170° that the whole of the nitrobenzene was removed.

The substance is sparingly soluble in boiling chloroform; on cooling the concentrated solution it separates in yellow prisms. In this case also the solvent adheres to the solid; it can be removed, however, by heating in the steam-oven for several hours, or, more readily, by keeping for a short time in an air-bath at 110—120°:

0·2053 gave 0·6588 $CO_2$ and 0·0870 $H_2O$. C=87·52; H=4·70.
0·2044 „ 0·6558 $CO_2$ „ 0·0875 $H_2O$. C=87·51; H=4·76.
$C_{31}H_{20}O_2$ requires C=87·73; H=4·72 per cent.

The *spiro*pyran compound dissolves readily in cold concentrated sulphuric acid, yielding a solution which appears deep red by transmitted light, and shows a very strong, deep green fluorescence.

### *The Anhydride of* 3:4-*Diphenyl*-2:5-*di*-β-*hydroxy*-α-*naphthylidene*-$\Delta^{3:4}$-cyclo*pentenone.* (*Diphenylacetylenedi*-β-*naphtha*spiro*pyran*) (IV).

This substance is readily obtained by the method employed in the case of the above *spiro*-compound, namely, by the action of hydrogen chloride on the mixture of the *cyclo*pentenone (2 grams) and β-naphthol-α-aldehyde (3 grams), dissolved in glacial acetic acid. The aldehyde was obtained for this purpose by means of the elegant method given by Gattermann for the preparation of aromatic aldehydes (Gattermann and von Horlacher, *Ber.*, 1899, **32**, 285).

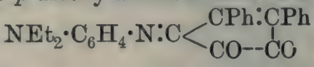
The brown solid which is deposited when the mixture is allowed to remain for two days, dissolves fairly readily in boiling chloroform, but only sparingly in hot alcohol; it crystallises from the mixed solvents, on cooling, in brown prisms, which darken at 265° and are completely charred at 280°. The substance is quite insoluble in potassium hydroxide, even on boiling. For analysis, the compound was dried in an air-bath at 120°:

0·1993 gave 0·6510 $CO_2$ and 0·0795 $H_2O$. C = 89·13; H = 4·43.

$C_{39}H_{24}O_2$ requires C = 89·31; H = 4·58 per cent.

Like the above, this *spiro*-compound dissolves in cold concentrated sulphuric acid to a deep red solution, which shows an intense green fluorescence.

### *Action of* p-*Nitrosodiethylaniline on* 3:4-*Diphenyl*cyclo*pentenone.*

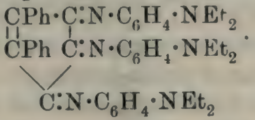
As already stated (p. 552), this reaction has been studied with the object of ascertaining whether 5-*p*-diethylaminoanilo-3:4-diphenyl-$\Delta^{3:4}$-*cyclo*pentene-1:2-dione,  $\mathrm{NEt_2\cdot C_6H_4\cdot N{:}C}\Big<\begin{array}{l}\mathrm{CPh{:}CPh}\\ \mathrm{CO{-}{-}CO}\end{array}$, behaves similarly to the corresponding compound, previously obtained (Ruhemann and Naunton, T., 1912, **101**, 42) from nitrosodimethylaniline, which in solution readily passes into the colloidal state.

The *cyclo*pentenone (5 grams) condenses with *p*-nitrosodiethylaniline (12 grams) when a little alcoholic potassium hydroxide is added to the mixture of the reagents dissolved in alcohol. On keeping for several days, a dark brown solid (6—7 grams) separates; this is sparingly soluble in cold, but fairly readily in boiling alcohol, forming a reddish-violet solution, which, on cooling, deposits violet-brown needles melting gradually at 170—171°:

0·2006 gave 0·5915 $CO_2$ and 0·1348 $H_2O$. C = 80·44; H = 7·46.
0·1567 „ 16·8 c.c. $N_2$ at 20° and 751 mm. N = 12·0.

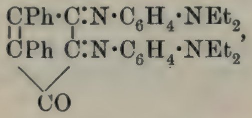
$C_{47}H_{52}N_6$ requires C = 80·57; H = 7·43; N = 12·0 per cent.

The analytical results indicate that the compound is 1:2:3-*tris-diethylaminoanilo*-4:5-*diphenyl*-$\Delta^{4:5}$-cyclo*pentene*,



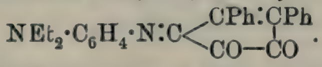
It corresponds, therefore, with the trisanilino-compound previously obtained by the action of nitrosodimethylaniline (*loc. cit.*), and its formation may be explained by the hypothesis already brought forward to account for the production of the latter compound.

It may be expected that, as in the case of the reaction between nitrosodimethylaniline and the *cyclo*pentenone, a second condensation product,



formed by the interaction of the ketone and two molecules of nitrosodiethylaniline, is produced at the same time as the tris-diethylaminoanilo-compound; this substance may be contained in the mother liquor of the latter, which was not further examined.

### 5-p-*Diethylaminoanilo*-3:4-*diphenyl*-$\Delta^{3:4}$-cyclo*pentene*-1:2-*dione*,



The violet compound, $C_{47}H_{52}N_6$, is easily decomposed by mineral acids (compare the behaviour of the analogous substance, $C_{41}H_{40}N_6$, *loc. cit.*), yielding a yellow solid, which, on warming with water, turns red. This substance is very soluble in chloroform, and moderately so in hot alcohol, from which it crystallises on cooling in red plates melting at 217—218°:

0·2062 gave 0·5980 $CO_2$ and 0·1125 $H_2O$. C = 79·05; H = 6·00.
0·2225 ,, 14·0 c.c. $N_2$ at 20° and 747 mm. N = 7·06.
$C_{27}H_{24}O_2N_2$ requires C = 79·41; H = 5·88; N = 6·86 per cent.

The compound forms a hydrochloride, which dissolves readily in alcohol; on addition of platinic chloride to the solution, a *platinichloride* is precipitated in yellow needles:

0·1461 gave 0·0233 Pt. Pt = 15·94.
$(C_{27}H_{24}O_2N_2)_2,H_2PtCl_6$ requires Pt = 15·86 per cent.

The compound $C_{27}H_{24}O_2N_2$ differs from the corresponding azomethine which is formed from nitrosodimethylaniline, in that its solutions in alcohol or chloroform do not yield gels.

### *Action of* iso*Amyl Formate on β-Hydrindone.*

The β-hydrindone required for the following experiments was obtained, as in the recent research on triketohydrindene hydrate (T., 1911, **99**, 796), from 1-chloro-2-hydroxyhydrindene, according to the directions given by Heusler and Schiefer (*Ber.*, 1899, **32**, 28). On adding the solution of the ketone (5 grams) and *iso*amyl formate (8·8 grams) in absolute ether to sodium ethoxide (5·2 grams) suspended in ether, the whole being cooled to 0°, a blue coloration develops. After three days, the mixture is shaken with ice-water; a viscous product, insoluble in ether or water, separates out. The clear aqueous layer, on treatment with acetic acid, yields a red oil, from which no solid product could be extracted; nor could any crystalline substance be obtained from the original dark, ethereal extract. It follows, therefore, that no hydroxymethylene derivative of β-hydrindone is formed under these conditions, the ketone being completely decomposed.

### *Formation of* spiro*Pyran Compounds from β-Hydrindone.*

2-Hydrindone, like diphenyl*cyclo*pentenone, reacts both with salicylaldehyde and with 2-naphthol-1-aldehyde, yielding *spiro*pyran compounds.

### *The Anhydride of* 1:3-*Disalicylidene*-2-*hydrindone* (*Phenylene-dibenzo*spiro*pyran*), (V).

When the alcoholic solution of the hydrindone (2 grams) and salicylaldehyde (3·1 grams) is saturated with hydrogen chloride at 0°, the liquid sets after a short time to a red, semi-solid mass, which cannot be separated by filtration; it is therefore allowed to dry on a porous plate. The substance is sparingly soluble in hot alcohol, more readily in boiling chloroform; on cooling, it separates from the latter solvent in deep red prisms, which melt gradually at 260—261°.

For analysis the substance must be freed from traces of chloroform by heating in an air-bath to 115—120°; the solvent adheres to the compound to such an extent that prolonged heating in the steam-oven is necessary to remove it:

0·1582 gave 0·4980 $CO_2$ and 0·0610 $H_2O$. C=85·85; H=4·28.

$C_{23}H_{14}O_2$ requires C=85·71; H=4·35 per cent.

The solution of this substance in cold concentrated sulphuric acid appears brown by transmitted light; it shows a green fluorescence, which is not quite so strong as that observed with the corresponding compound obtained from diphenyl*cyclo*pentenone.

### *The Anhydride of* 1:3-*Di-β-hydroxy-α-naphthylidene-2-hydrindone* (*Phenylenedi-β-naphtha*spiro*pyran*) (VI).

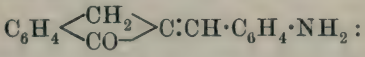
This octacyclic *spiro*pyran compound is prepared by the method employed in the case of the above substance. On treatment of the alcoholic solution of the ketone (2 grams) and 2-naphthol-1-aldehyde (5·8 grams) with hydrogen chloride at 0°, a deep blue coloration is developed, and a black solid is deposited. After two hours, this is collected and washed with alcohol, in which it is insoluble. It dissolves in boiling glacial acetic acid to a reddish-violet solution, from which it separates slowly on cooling in small, bluish-black prisms, which undergo no perceptible change on being heated to 320°. For analysis the substance was dried at 120°:

0·1978 gave 0·6395 $CO_2$ and 0·0745 $H_2O$. C=88·17; H=4·18.
$C_{31}H_{18}O_2$ requires C=88·15; H=4·27 per cent.

The solution of this compound in cold concentrated sulphuric acid is deep red and only faintly fluorescent; on boiling, however, an intense fluorescence is developed.

### *The Action of* o-*Aminobenzaldehyde on* 1-*Hydrindone.*

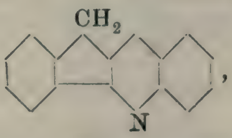
This reaction occurs on addition of a few drops of alcoholic potassium hydroxide to the mixture of the aldehyde (4·5 grams) and the hydrindone (5·1 grams), dissolved in alcohol. The solution becomes red, and after a few minutes a yellow solid separates. This is sparingly soluble in cold alcohol, moderately so in boiling, and crystallises on cooling in orange prisms melting at 202—205°. The compound is 2-o-*aminobenzylidene*-1-*hydrindone*,



$$C_6H_4{<}{\overset{CH_2}{\underset{CO}{}}}{>}C{:}CH{\cdot}C_6H_4{\cdot}NH_2:$$

0·2087 gave 0·6240 $CO_2$ and 0·1080 $H_2O$. C=81·54; H=5·75.
0·2265 „ 12·2 c.c. $N_2$ at 17° and 746 mm. N=6·13.
$C_{16}H_{13}ON$ requires C=81·70; H=5·53; N=5·96 per cent.

In addition to 2-*o*-aminobenzylidene-1-hydrindone, indenoquinoline,



is formed in this reaction. This substance is obtained in the mother liquor after the separation of the above compound, and is precipitated as a white solid on the addition of water. It crystallises from dilute alcohol in colourless needles melting at 170—171°:

0·2080 gave 0·6745 $CO_2$ and 0·0940 $H_2O$. C=88·44; H=5·13.
0·2095 „ 11·8 c.c. $N_2$ at 18° and 761 mm. N=6·61.
$C_{16}H_{11}N$ requires C=88·48; H=5·07; N=6·45 per cent.

The same compound is formed, also, if a little concentrated hydrochloric acid is added to 2-*o*-aminobenzylidene-1-hydrindone dissolved in alcohol, and the solution evaporated to small bulk on the water-bath. In the course of a few hours, colourless needles of the hydrochloride of the quinoline separate. This salt is unstable, and gradually dissociates, on boiling with water, into hydrochloric acid and the free base; but if platinic chloride is added to the alcoholic solution a light yellow platinichloride is precipitated, which decomposes at about 270°:

0·2320 gave 0·0535 Pt. Pt=23·06.
$(C_{16}H_{11}N_2)_2,H_2PtCl_6$ requires Pt=23·05 per cent.

Indenoquinoline was obtained by Noelting and Blum (*Ber.*, 1901, **34**, 2471), who described it under the name quinolylenephenylenemethane. These authors prepared the compound by the distillation of the corresponding ketoindenoquinoline with a mixture of zinc and zinc oxide; they gave the melting point as 166—167°, and fixed the composition by a nitrogen determination only.

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## LXIV.—*Partially Methylated Glucoses. Part I. ζ-Monomethyl Glucose and γεζ-Trimethyl Glucose.**

By James Colquhoun Irvine and James Patterson Scott, M.A., D.Sc. (Carnegie Fellow).

Derivatives of sugars in which only some of the hydroxyl groups are substituted are, of course, well known, but in many cases it is probable that substances of this nature described in the literature

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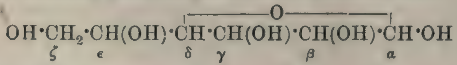
* The method adopted in this and the succeeding paper to indicate the position of substituting groups in the sugar molecule differs from that hitherto in use, as the carbon atom of the reducing group is now indexed as the α-atom.



$$\underset{\zeta}{\mathrm{OH{\cdot}CH_2}}{\cdot}\underset{\epsilon}{\mathrm{CH(OH)}}{\cdot}\overbrace{\underset{\delta}{\mathrm{CH}}{\cdot}\underset{\gamma}{\mathrm{CH(OH)}}{\cdot}\underset{\beta}{\mathrm{CH(OH)}}{\cdot}\underset{\alpha}{\mathrm{CH}}}^{\mathrm{O}}{\cdot}\mathrm{OH}$$

It will be seen that the oxygen ring-system (invariably termed the "γ-oxidic ring") now connects the α- and δ-atoms, and thus all references in previous papers to the position of substituting groups are rendered inaccurate (see T., 1913, **103**, 41, 243; 1912, **101**, 1128, 1146; *Ann. Reports*, 1912, **9**, 95).

The authors wish it to be understood that they are not responsible for this inconsistency (see P., 1913, **29**, 69).

are merely mixtures and not individual compounds; thus, complete series of acetylated and benzoylated glucoses have been at various times described, but, considering the methods of preparation and the nature of the products, it is difficult to imagine that definite compounds were isolated. In general, the action on a sugar of excess of a reagent, which attacks hydroxyl groups, is to give a fully substituted derivative, whilst with restricted proportions of the same reagent, complex mixtures are formed which, as a rule, cannot be completely separated. This has naturally imposed limitations on the study of the individual asymmetric systems of the sugar molecule.

The hydroxyl groups in glucose may be differentiated into three classes, namely, (1) the reducing group, (2) the three remaining secondary alcohol groups, and (3) the terminal primary alcohol group. The first-mentioned group takes part in glucoside formation, and its special reactivity is also shown in many other reactions. Until recently, there seemed little necessity to distinguish sharply between the classes (2) and (3) mentioned above, but the preparation by Fischer of derivatives of ζ-aminoglucose (*Ber.*, 1912, **45**, 3763) involves a striking instance of the special reactivity of the primary alcohol group. It is possible that the study of the sugars may be profitably extended, and the significance of configuration may become more fully apparent by examination, as far as possible, of the characteristics of each individual hydroxyl group present in the molecule and of the asymmetric system to which it belongs. It is with this object in view that we have undertaken the examination of a series of partly methylated glucoses.

In compounds of the type of tetramethyl glucose, the reactivity of the molecule is practically confined to the reducing group. On the other hand, in a partly methylated glucose the characteristic properties of the parent sugar are more closely preserved, and a greater variety of reactions are available. Moreover, owing to the increase of stability and solubility due to methylation, the more obscure decompositions undergone by unsubstituted sugars are, to a large extent, precluded.

The general method devised by Purdie and Irvine for the alkylation of sugars does not admit of the isolation of incompletely substituted derivatives other than compounds of the nature of βγε-trimethyl glucose. In the first paper of the series, however, (T., 1903, **83**, 1021) it was pointed out that, in order to protect a sugar from oxidation during the silver oxide reaction, all that is necessary is to substitute the reducing group by a condensed residue capable of subsequent removal by hydrolysis. For obvious reasons, compounds of the nature of methylglucoside have been largely made use of for this purpose, but other types of sugar derivatives may also be employed. Of these, the compounds produced by the condensation of sugars with ketones or aldehydes are best adapted for the purpose required; for example, a glucosidic monoacetone derivative of a hexose must, irrespective of the linking of the acetone residue, contain three hydroxyl groups capable of methylation, so that hydrolysis of the alkylated product should give a trimethyl hexose; similar treatment of a diacetone derivative should result in a monomethylated aldose or ketose. The remaining type of a partly methylated hexose would be represented by a dimethyl glucose, and this has now been prepared, as described in the succeeding paper, by alkylation of benzylidene methylglucoside, and removal of benzaldehyde and methyl alcohol by hydrolysis.

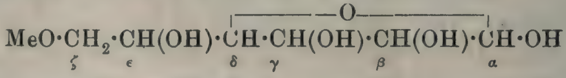
The principles outlined above have already been applied to the preparation of dimethyl rhamnose and monomethyl fructose (T., 1906, **89**, 1194; 1909, **95**, 1220), and are of wide application. It is thus possible, by the introduction of hydrolysable residues into the sugar molecule, to protect selected hydroxyl groups from alkylation. The process is also applicable to the preparation of similar derivatives from polyhydric alcohols.

The following table summarises the methods adopted in the preparation of the different types of methylated glucoses now known:

| Condensed glucose derivative. | Number of methoxyl groups added. | Groups removed by hydrolysis. | Methylated glucose formed. |
|---|---|---|---|
| Glucosediacetone ......... | 1 | Two mols. acetone | Monomethyl glucose |
| Benzylidene α-methylglucoside .................. | 2 | Methyl alcohol and benzaldehyde | Dimethyl glucose |
| Glucosemonoacetone ...... | 3 | One mol. acetone | Trimethyl glucose |
| Methylglucoside ............ | 4 | Methyl alcohol | Tetramethyl glucose |

### ζ-*Monomethyl Glucose.*

The constitution assigned to this compound will be discussed later, and it will be shown that the methoxyl group is most probably attached to the terminal carbon atom in the sugar chain, that is, in the position marked ζ in the following formula:



$$MeO\cdot\underset{\zeta}{CH_2}\cdot\underset{\epsilon}{CH(OH)}\cdot\overbrace{\underset{\delta}{CH}\cdot\underset{\gamma}{CH(OH)}\cdot\underset{\beta}{CH(OH)}\cdot\underset{\alpha}{CH}}^{O}\cdot OH$$

The compound may therefore be termed ζ-monomethyl glucose. The method of preparation was to methylate glucosediacetone by means of the silver oxide reaction, with the precautions found advisable in the case of the corresponding fructose derivative. The product consisted of monomethyl glucosediacetone, which was purified by fractional distillation (b. p. 139—140°/12 mm.). The properties and solubilities of this compound resembled those of other methylated sugar derivatives of a glucosidic nature, but the fact that it is lævorotatory ($[\alpha]_D$ $-32{\cdot}2°$ in alcohol) is worthy of note.

The removal of the acetone residues by hydrolysis took place with extreme ease. The course of the reaction was followed polarimetrically, and the results showed that both acetone groups were removed simultaneously and at apparently the same rate. The product of this reaction was monomethyl glucose, which showed all the characteristic properties of a reducing sugar. When crystallised from a mixture of methyl alcohol and acetone, the compound showed downward mutarotation, and this form is accordingly regarded as the α-isomeride. The β-form of the sugar, showing upward mutarotation, was isolated by the method described in the experimental part. The mutarotatory changes shown by both forms in methyl alcoholic solution were:

| Initial $[\alpha]_D^{20°}$ of α-form. | | Permanent $[\alpha]_D^{20°}$. | | Initial $[\alpha]_D^{20°}$ of β-form. |
|---|---|---|---|---|
| $+98{\cdot}6°$ | $\longrightarrow$ | $+68{\cdot}0°$ | $\longleftarrow$ | $+29{\cdot}6°$ |

The nature of the solvent had very little effect on the magnitude of the initial rotations, and as the sugar showed suspended mutarotation in methyl alcohol it was possible to obtain accurate values for the initial readings. The above data, calculated in the form of molecular rotations, may thus be applied to test the generalisations established by C. S. Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 66) regarding rotatory power in the sugar group. If A and B represent the proportion of the molecular rotation due respectively to the reducing group and the remainder of the molecule, we have:

| | |
|---|---|
| Monomethyl α-glucose......... | $[M]_D = 19128 = +A + B$ |
| Monomethyl β-glucose......... | $[M]_D = 5752 = -A + B$. |

In this particular case, the sum (2B) should be different from the similar value obtained for glucose as the non-reducing part of the molecule is different. On the other hand, the difference (2A) should be identical. The figures are compared below:

| | Sum (2B). | Difference (2A). |
|---|---|---|
| Glucose ........................ | 23040 | 16200 |
| Monomethyl glucose......... | 24880 | 13376 |

The agreement with the calculated values is thus only approximate; in fact, the differences are proportionally more divergent than the sums. Possibly a closer agreement is not to be expected, as Hudson's rule is based on the assumption that the principle of optical superposition holds exactly. At the same time, it will be shown in the succeeding paper that the optical values for dimethyl glucose show a much closer agreement with the figures calculated by Hudson's method. It would thus appear that his generalisation applies, approximately at least, to sugars in which the hydroxyl positions are methylated. Doubtless the values we ascribe to the initial rotations of monomethyl β-glucose are not strictly accurate. The α-form was certainly obtained in the pure state, but this cannot be claimed for the β-isomeride, which was only isolated in small amount. Accordingly, if the difference (2A) be adjusted to the calculated value (16,200), the theoretical initial specific rotation for the β-form becomes +15·1°, in place of the recorded value +29·6°.

Extending these considerations to other methylated glucoses we find, as stated, that Hudson's rule applies to dimethyl glucose. Unfortunately, trimethyl glucose has only, so far, been obtained as a syrup, and all our attempts to isolate the pure β-form of tetramethyl glucose failed. If, however, the validity of Hudson's method be accepted, the initial specific rotation of βγεζ-tetramethyl β-glucose becomes +32·16°. The adoption of this value can be justified on other grounds, as the specific rotations of the α- and β-tetramethyl methylglucosides are known. Now, in comparing a sugar with its glucosides, the sum (2B) should be constant, whilst the difference (2A) should vary. The value for 2B should thus be identical for the fully alkylated glucosides and tetramethyl glucose. This is shown below to be essentially the case.

*Sum of Molecular Rotations.*

| | |
|---|---|
| Tetramethyl methylglucosides | 32515 (found) |
| Tetramethyl glucoses ............ | 31380 (value for the β-form calculated). |

The discrepancy is thus slightly over 3 per cent., which is well within the limits of the experimental error. The following table gives the corrections of some of our experimental results indicated by applying Hudson's method:

| | Found. | Calculated. |
|---|---|---|
| ζ-Monomethyl β-glucose .................. | $[\alpha]_D$ +29·6° | +15·1 |
| βγεζ-Tetramethyl β-glucose............... | (not isolated) | +32·16 |
| βγ-Dimethyl α-glucose ...................... | +81·93 | +83·80. |

*Constitution of Monomethyl Glucose.*

The sugar resembled monomethyl fructose in general properties, and was converted into the same monomethylglucosazone. This at once indicates that the methyl group is attached to the terminal carbon atom. It should be stated, however, that the constitution of monomethyl fructose is not rigidly established, as the evidence afforded by oxidation is capable of a double interpretation. The methyl group may, in fact, be situated either in the $\gamma$ or $\zeta$ positions. The former alternative is, however, completely at variance with the results obtained in the study of the isomeric fructose monoacetones (T., 1910, **97**, 1277), and is in the meantime unsupported by any positive evidence.

### $\gamma\epsilon\zeta$-*Trimethyl Glucose.*

One form of a trimethyl glucose (*loc. cit.*, and T., 1903, **83**, 1037), in which the methyl groups are present in positions $\beta\gamma\epsilon$, has already been described. In the course of the present research, the isomeric $\gamma\epsilon\zeta$-trimethyl glucose was also prepared.

Glucosemonoacetone, on complete methylation, was converted into trimethyl glucosemonoacetone (b. p. 138—139°/12 mm.). The isolation of the liquid product was accompanied by slight hydrolysis of the acetone residue, so that the optical values have little significance, but the fact that the compound is lævorotatory is nevertheless remarkable. The hydrolysis was carried out in the usual manner, but as the sugar could not be obtained crystalline the syrup examined consisted of a mixture of $\alpha$- and $\beta$-forms in equilibrium. The proportion of the $\beta$-form was, however, increased by heating the compound at 70°, after which, on solution in alcohol, the following optical change was shown:

| Initial specific rotation. | | Permanent specific rotation. |
|---|---|---|
| $-6{\cdot}2°$ | $\longrightarrow$ | $-8{\cdot}3°$. |

The rotatory power of this sugar is in every respect abnormal. Whereas both the $\alpha$- and $\beta$-forms of glucose, and also of all other known methylated glucoses, are dextrorotatory, the equilibrium value for $\gamma\epsilon\zeta$-trimethyl glucose is lævorotatory. Not only so, but the mutarotation recorded above indicates that the $\alpha$-form is also lævorotatory, as the change $\beta \longrightarrow \alpha$ results in an increase of rotation in the lævo-sense. This is at variance with all other optical values obtained for the glucoses, and admits of no simple explanation. The preparation of the sugar has been repeated on two occasions by independent workers, who have verified our results, and the possibility that methylation in the $\gamma$-position of the glucose molecule is attended with great alterations in rotatory power is being further investigated by one of us (Dr. Scott).

## EXPERIMENTAL.

### *Preparation of Glucosediacetone and Glucosemonoacetone.*

Considerable difficulty was experienced in preparing a sufficient quantity of glucosediacetone, and accordingly the directions given by Fischer (*Ber.*, 1895, **28**, 1145, 2496) were modified. All the operations involved in converting the sugar into the corresponding dimethylacetal were conducted in Winchester bottles, so that the syrupy product could afterwards be thoroughly incorporated with the acetone used in the subsequent condensation. In each experiment, 30 grams of glucose were used, and the crude dimethylacetal was obtained in the form of a syrup adhering to the sides of the bottle. Fragments of porous tile were added, and the mixture was vigorously shaken for six hours with a large excess of acetone containing 0·25 per cent. of hydrogen chloride. The solution was thereafter preserved for thirty-six hours in an incubator at 33°, with occasional periods of shaking. The free acid was then removed by means of silver carbonate, the solution shaken with charcoal, and the solvent removed in a vacuum.

In our experience, the syrup thus obtained consisted of a mixture of the di- and mono-acetone derivatives, the former being in excess, and crystallised completely on cooling. The solid mass was finely powdered and extracted repeatedly with a large excess of petroleum of low boiling point until all the glucosediacetone had been removed, after which the insoluble residue, consisting essentially of the monoacetone compound, was recrystallised from dry ethyl acetate. The two products were thus obtained in one operation, and, as the combined yield amounted to 30 per cent. of the glucose used, the efficiency of the process was practically doubled.

### *Methylation of Glucosediacetone.*

Owing to the ease with which the acetone residues are removed from glucosediacetone, several precautions were necessary in carrying out the methylation. The method actually adopted was essentially the same as that already described (*loc. cit.*) for the methylation of fructosediacetone by the silver oxide process, and the proportions of the reacting materials employed were identical. In isolating the methylated product it was found to be of the utmost importance to use ether free from traces of acid, and to avoid prolonged boiling with the solvent.

After drying the ethereal extract by means of sodium sulphate and removal of the solvent, the theoretical amount of a neutral oil remained, which was fractionated in a vacuum. After two distillations the main fraction boiled at 139—140°/12 mm., and consisted of pure monomethyl glucosediacetone.

Found: C=56·54; H=7·99; OMe=11·60.

$C_{12}H_{19}O_5(OMe)$ requires C=56·93; H=8·03; OMe=11·31 per cent.

The following observations were made on the optical activity of the substance:

| Solvent. | $c.$ | $l.$ | $\alpha_{20^\circ}$ | $[\alpha]_D^{20^\circ}$ |
|---|---|---|---|---|
| Ethyl alcohol............ | 5·05 | 2 | −3·25° | −32·17° |
| Acetone .................. | 5·02 | 2 | 3·19 | 31·78 |

*Monomethyl glucosediacetone* is a colourless, mobile, highly refractive liquid, which has no action on Fehling's solution until after hydrolysis. The compound is readily soluble in the ordinary organic solvents, but only sparingly so in water. On heating a solution of the compound in 50 per cent. alcohol, containing 0·1 per cent. of hydrogen chloride at 80°, the acetone groups were completely removed in twelve hours. During this time the rotation altered regularly from lævo to dextro, and, as the curve representing the change showed no break, it may be concluded that both ketonic residues are removed simultaneously and at the same rate.

### *Monomethyl Glucose.*

A 5 per cent. solution of monomethyl glucosediacetone in a large excess of 50 per cent. aqueous alcohol containing 0·4 per cent. of hydrogen chloride was heated in boiling water for one hundred and five minutes. The acid was removed with silver carbonate, after which the solution was shaken with charcoal, filtered, and evaporated to a syrup at 35°/15 mm. The residue was then dissolved in methyl alcohol, and the solution allowed to evaporate spontaneously in a vacuum desiccator. After twelve hours, monomethyl glucose commenced to separate in the form of a crystalline crust and the bulk of the product was isolated by the addition of acetone to the solution, a procedure which promoted the separation of the $\alpha$-form in excess. The yield of crystalline product was 50 per cent. of the monomethyl glucosediacetone used in the hydrolysis.

Found: C=43·24; H=7·13; OMe=15·74.

$C_6H_{11}O_5(OMe)$ requires C=43·30; H=7·22; OMe=15·98 per cent.

*Monomethyl glucose* is readily soluble in water, less so in methyl alcohol, and very sparingly soluble in other organic solvents. It reduces Fehling's solution readily on warming.

### *Isolation of $\alpha$- and $\beta$-Forms of Monomethyl Glucose.*

When the sugar was crystallised from methyl alcoholic solution only the $\alpha$-form separated. The product thus obtained crystallised in short, rectangular plates, which melted sharply at 157—158°, and showed extensive mutarotation in aqueous solution. The same form of the sugar was precipitated in the crystalline state by the cautious addition of acetone to a methyl-alcoholic solution, but, as afterwards explained, successive crops are liable to contain increasing amounts of the β-form.

### *Mutarotation of ζ-Monomethyl α-Glucose.*

| Solvent. | *c.* | Mutarotation. |
|---|---|---|
| Water.................... | 2·424 | $+96{\cdot}7^\circ \longrightarrow +55{\cdot}5^\circ$ |
| Methyl alcohol ........ | 1·084 | $98{\cdot}6 \longrightarrow 68{\cdot}0$ |

Equilibrium was established very rapidly in aqueous solution, and the permanent rotation was recorded eleven minutes after the first reading.* On the other hand, the compound exhibited suspended mutarotation in methyl alcohol, and the change was only apparent on the addition of a trace of alkali.

*ζ-Monomethyl β-Glucose.*—A 30 per cent. solution of the α-form of the sugar in methyl alcohol was boiled under a condenser until the equilibrium $\alpha \rightleftharpoons \beta$ had been established. The bulk of the solvent was then removed at the ordinary pressure until a mobile syrup remained. On adding small quantities of acetone, the sugar in solution was precipitated in two fractions, the first of which consisted entirely of the α-form. The more soluble crop was a mixture of both isomerides, whilst the mother liquor deposited crystalline nuclei of the β-form.

The process described above was therefore repeated, and the bulk of the α-sugar precipitated as usual. After filtration, nuclei of the β-form were added to the filtrate, and a small, apparently homogeneous crop of the β-isomeride separated.

*Monomethyl β-glucose* crystallises in delicate, prismatic needles, which are extremely soft and friable, and melt at 130—132°. The mutatory changes observed are given below:

| Solvent. | *c.* | Initial $[\alpha]_D^{20^\circ}$. Final $[\alpha]_D^{20^\circ}$. |
|---|---|---|
| Water........................ | 1·080 | $+31{\cdot}9^\circ \longrightarrow +55{\cdot}1^\circ$ |
| Methyl alcohol ......... | 1·080 | $28{\cdot}0 \longrightarrow 68{\cdot}0$ |

The end-points are thus in satisfactory agreement with those recorded for the α-form.

### *ζ-Monomethyl Methylglucoside.*

This compound was prepared by Fischer's process, a 5 per cent. solution of monomethyl glucose in methyl alcohol containing 0·25 per cent. of hydrogen chloride, being heated for sixty hours at 100°. The product was worked up in the usual manner, and was isolated as a viscous syrup, for which no crystallising medium could be found. The compound was ultimately analysed without further purification. During the dehydration of the analysis sample constant weighings were only obtained after heating for five hours in a vacuum at 100°. This treatment apparently effected some decomposition, as the analytical figures obtained were only approximate.

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* The speed of this change suggests that a catalyst was accidentally present.

Found: $C=46{\cdot}70$; $H=7{\cdot}79$; $OMe=27{\cdot}0$.

$C_6H_{10}O_4(OMe)_2$ requires $C=46{\cdot}15$; $H=7{\cdot}69$; $OMe=29{\cdot}8$ per cent.

*Monomethyl methylglucoside* is extremely soluble in water, and the usual organic solvents with the exception of hydrocarbons. It behaves as a glucoside towards Fehling's solution, and shows, for $c=1{\cdot}973$, $[\alpha]_D +99{\cdot}3°$ in ethyl alcohol. This value has little significance, as it is determined on the equilibrium mixture of the $\alpha$- and $\beta$-forms.

### ζ-*Monomethylglucosazone.*

The methylated sugar was dissolved in the minimum amount of 50 per cent. acetic acid, and mixed with a slight excess of phenylhydrazine acetate similarly dissolved. On heating the solution to 100° for three or four minutes and cooling, an abundant crop of yellow needles separated. After crystallisation from aqueous alcohol the compound melted at 164—165°, and analysis showed it to be monomethylglucosazone.

Found: $C=61{\cdot}05$; $H=6{\cdot}72$; $OMe=7{\cdot}0$.

$C_{18}H_{21}O_3N_4(OMe)$ requires $C=61{\cdot}21$; $H=6{\cdot}45$; $OMe=8{\cdot}3$ per cent.

The similarity of the osazone with that previously isolated from monomethyl fructose (*loc. cit.*) was so great as to suggest the identity of the two compounds, although the melting point now found was considerably higher. The value quoted in our previous paper was 142—144°, but this seems due to a clerical error. Fortunately, some of the original osazone was available for comparison. Both preparations, when examined under parallel conditions, melted at the same temperature (164°), and a mixture of the two gave the same melting point. As the specific rotation in ethyl alcohol ($[\alpha]_D -86{\cdot}7°$ for $c=0{\cdot}5$) was also the same for each compound, there is no doubt that the two preparations are identical.

### γεζ-*Trimethyl Glucose.*

*Methylation of Glucosemonoacetone.*—Before methylation, the glucosemonoacetone was twice recrystallised from neutralised ethyl acetate. It then melted at 154—155°, and showed $[\alpha]_D -9{\cdot}6°$ in aqueous solution, values which differ slightly from those quoted by Fischer. The same precautions were adopted during the methylation as were employed in the case of glucosediacetone.

A 6 per cent. solution of the monoacetone compound (1 mol.) in dry acetone was mixed with methyl iodide (6 mols.), and silver oxide (3 mols.) gradually added. The reaction, which was at first vigorous, was continued by boiling gently on a water-bath for five hours. After extraction of the product with ether and removal of the solvent in a vacuum, a colourless syrup remained, which was freely soluble in methyl iodide. No extraneous solvent was thus required in the second methylation, in which the proportion of alkylating mixture was doubled. The product, isolated in the usual manner, was distilled under diminished pressure, and subjected to a third methylation, after which the main fraction boiled at 138—139°/12 mm. Contrary to expectation, the yield of volatile material was small, and a considerable residue remained behind in the flask. Moreover, the distilled liquid had acquired a perceptible action on Fehling's solution. It was thus evident that hydrolysis had taken place to some extent during the distillation, and this view was confirmed by analysis.

Found: $C=53·52$; $H=8·17$; $OMe=37·98$.
$C_9H_{13}O_3(OMe)_3$ requires $C=54·96$; $H=8·17$; $OMe=35·50$ per cent.

The results are thus intermediate between those calculated for trimethyl glucosemonoacetone and its hydrolysis product.

Solvent: methyl alcohol, $c=3·77$, $[\alpha]_D\ -27·2°$.

*Hydrolysis of Trimethyl Glucosemonoacetone.*—On heating a dilute solution of the above compound in aqueous alcohol containing 0·5 per cent. of hydrogen chloride for seventy-five minutes at 100°, the lævo-rotation diminished to a constant value. The further treatment was as usual, and the resulting colourless syrup, which could not be rendered crystalline, was analysed after drying at 70°/15 mm. until constant in weight.

Found: $C=49·12$; $H=8·11$; $OMe=42·0$.
$C_6H_9O_3(OMe)_3$ requires $C=48·75$; $H=8·11$; $OMe=41·9$ per cent.

The sugar, which is very soluble in water and in organic solvents, reduces Fehling's solution actively. The following observations on the optical activity of the substance were made on a specimen which had been heated for forty-five minutes at 70°:

| Solvent. | *c.* | *l.* | Initial $[\alpha]_D^{20°}$. | Final $[\alpha]_D^{20°}$. |
|---|---|---|---|---|
| Water............ | 4·39 | 2 | $-7·52°$ → | $-8·32°$ |
| Ethyl alcohol.. | 4·67 | 2 | 6·20 → | 8·34 |

No crystalline derivative of the compound could be isolated. The sugar was resinified by phenylhydrazine and even condensation with aniline, which usually proceeds smoothly with methylated sugars, resulted in much decomposition. On account of the abnormal nature of this compound it is now being examined in greater detail.

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United College of St. Salvator and St. Leonard,
University of St. Andrews.

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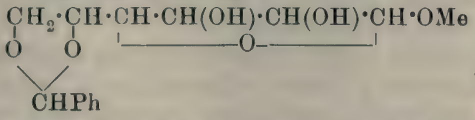
# LXV.—*Partially Methylated Glucoses. Part II. βγ-Dimethyl α-Glucose and βγ-Dimethyl β-Glucose.*

By James Colquhoun Irvine and James Patterson Scott, M.A., D.Sc. (Carnegie Fellow).

In continuation of the work described in the preceding paper, we have applied similar principles to introduce two methyl groups into glucose so as to give a reducing sugar. For the preparation of a dimethyl glucose of this nature, two of the hydroxyl groups in glucose, in addition to the reducing group, must be protected from methylation by the introduction of hydrolysable residues. Few substances of this type are available, but we have found that the benzylidene α-methylglucoside described by Alberda van Ekenstein (*Rec. trav. chim.*, 1906, **25**, 153) is well adapted for the purpose.

It will afterwards be shown that the most probable structure for the latter compound is that given below:



$$\mathrm{CH_2\cdot CH\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot OMe}$$

According to this view of the constitution, the formation of the compound involves the introduction of a new asymmetric system into the molecule, and thus benzaldehyde should condense with α-methylglucoside so as to produce two isomeric products. This possibility seems to have been overlooked by Alberda van Ekenstein, but has been referred to by Fischer (*Ber.*, 1894, **27**, 1524). We have succeeded in isolating the hitherto unknown isomeride by cautious crystallisation of the accumulated mother liquors obtained in large scale preparations of the condensation compound. The new stereoisomeride crystallises in short prisms, melting at 148—149°, and shows $[\alpha]_D$ $+96{\cdot}0°$ in aqueous solution. This compound, which is produced in very small amount, is regarded as εζ-*d*-benzylidene α-methyl-*d*-glucoside.

The methylation of $\epsilon\zeta$-*l*-benzylidene $\alpha$-methylglucoside was carried out by the silver oxide reaction. No other process is, in fact, available, as the compound is exceedingly easily hydrolysed by acids, and also to some extent by alkalis. The alkylation proceeded with unusual smoothness. The product, which was readily obtained in the crystalline state, melted at 122—123°, and showed $[\alpha]_D + 97{\cdot}03°$ in acetone solution.

It was possible, by carefully regulated hydrolysis, to remove the aromatic residue without affecting the glucosidic group, the product of this reaction being $\beta\gamma$-dimethyl $\alpha$-methylglucoside, which was isolated in the usual manner. The alkylated glucoside melted at 80—82°, and showed practically the same specific rotation (142·6°) in aqueous and in acetone solution. When boiled with dilute hydrochloric acid, the glucosidic group was removed with the formation of dimethyl glucose, which was isolated in the form of a crystalline solid. After crystallisation from ethyl acetate, the sugar separated in well-developed prisms, which gave satisfactory analytical figures, but which melted very indefinitely. This behaviour was shown to be due to the presence of the stereoisomeric $\alpha$- and $\beta$-forms, both of which were ultimately isolated.

When the crystallisation from ethyl acetate was carried out from solutions containing not more than 5 per cent. of the solute, the sugar separated in clusters of delicate, pointed prisms. This proved to be the pure $\beta$-form (m. p. 108—110°), and thus showed upward mutarotation when dissolved in water, alcohol, or acetone. The details of these optical changes are given in the experimental part. The sugar exhibited suspended mutarotation in acetone solution, and it was therefore possible to obtain an exact record of the whole range of the change in this solvent.

The $\alpha$-form of the sugar crystallised, along with the $\beta$-isomeride, from solutions in ethyl acetate containing from 7 to 10 per cent. of the solute. Separation of the two varieties was, however, best effected by cautious precipitation, from the equilibrium solution in alcohol, by the gradual addition of ether. The first crops to separate consisted, as before, of the $\beta$-form, but, from the mother liquors, the $\alpha$-isomeride (m. p. 85—87°) was deposited in warty aggregates of microscopic prisms. This form showed extensive downward mutarotation in acetone solution.

Dimethyl glucose is thus well adapted for the study of mutarotation, as both stereoisomeric forms are available, and the ready solubility of the sugar, in solvents in which the change is slow, permits of the initial values being determined with much greater accuracy than in the case of an unsubstituted sugar.

### *Discussion of Optical Results.*

The specific rotations of dimethyl glucose and its derivatives are only very slightly affected by the nature of the solvent employed. This is seen from the examples quoted below:

| Solvent. | $\beta\gamma$-Dimethyl $\beta$-Glucose. | $\beta\gamma$-Dimethyl $\alpha$-Methylglucoside. |
|---|---|---|
| Water | +5·7° | +142·64° |
| Alcohol | 5·7 | 143·08 |
| Acetone | 5·9 | 143·49 |

In this respect the compound resembles tetramethyl glucose, but the uniformity of the rotations in the different solvents is here even more marked. The nature of the solvent has, however, in the case of dimethyl glucose, a pronounced effect in altering the proportions of the mutarotatory $\alpha$- and $\beta$-forms which exist in equilibrium in solution. Thus, the equilibrium mixture in aqueous solution contains 77 per cent. of the $\alpha$-form and 23 per cent. of the $\beta$-isomeride. In acetone solution, on the other hand, the proportions are altered to 59 and 41 per cent. respectively.

Owing to the facility with which the true initial specific rotations of the $\alpha$- and $\beta$-forms of dimethyl glucose may be determined in acetone solution, the compound is a convenient one for testing the application of Hudson's rule (see preceding paper). The choice of acetone as a solvent for this purpose was determined by the facts, mentioned above, that the specific rotation of the sugar is practically unaffected by the nature of the solvent, and that the compound shows suspended mutarotation in this solvent. With regard to the accuracy of the optical values which we ascribe to the $\alpha$- and $\beta$-forms, there is little doubt that the latter isomeride was obtained in a pure condition, unmixed with the $\alpha$-form. On the other hand, the experimental difficulties encountered in isolating the $\alpha$-form were very great, and there is thus a possibility that the recorded specific rotation is lower than the true maximum. The discrepancy is, however, probably small.

Applying Hudson's principle, that the proportion of the molecular rotation of a sugar contributed respectively by the reducing group and the remainder of the molecule may be represented by $A$ and $B$, the following equations are derived:

$$\beta\gamma\text{-Dimethyl }\alpha\text{-glucose} \ldots\ldots\ldots \quad [M]_D = 17041 = +A + B$$
$$\beta\gamma\text{-Dimethyl }\beta\text{-glucose} \ldots\ldots \quad [M]_D = 1227 = -A + B$$

The sum of the molecular rotations ($2B$) thus equals 18268, and the difference ($2A$) equals 15814. The particular case now under consideration resembles that of monomethyl glucose, in that the value of $2B$ should differ from that determined for glucose, whilst, if Hudson's rule applies to substituted sugars, $2A$ should be a constant irrespective of the methylation of the non-reducing hydroxyl groups. These values are compared below:

| | Sum of Molecular Rotations ($2B$). | Difference of Molecular Rotations ($2A$). |
|---|---|---|
| Glucose............... | 23040 | 16200 |
| Dimethyl glucose.. | 18268 | 15814 |

It will thus be seen that the value actually found for $2A$ differs only by slightly over 2 per cent. from that calculated according to Hudson's method. Taking into consideration the fact that extreme accuracy cannot be claimed for the specific rotation of the α-form, the conclusion may reasonably be drawn that the generalisation is supported by this result. An alteration of the initial rotation of α-dimethyl glucose from $[\alpha]_D +81{\cdot}93°$ to $83{\cdot}80°$ would, in fact, give the calculated value (16200) for $2A$.

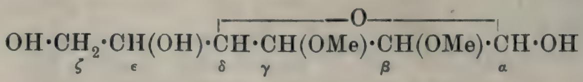
It may be mentioned that Hudson's method of calculation does not seem applicable to the case of the α- and β-forms of benzylidene methylglucoside, where the difference ($2A$) should equal that calculated from the activities of the methylglucosides. The values actually found are, however, far apart.

| | Sum ($2B$). | Difference ($2A$). |
|---|---|---|
| Methylglucosides ............... | 24371 | 36729 |
| Benzylidene methylglucosides | 2820 | 45120 |

The introduction of the new asymmetric ring system into the molecule seems to exclude the application of Hudson's rule, but a definite decision on this point must be withheld until both stereoisomeric forms of benzylidene β-methylglucoside have been isolated. From the comparatively small difference in rotation shown by *d*- and *l*-benzylidene α-methylglucoside, it is, however, most unlikely that any agreement will be found.

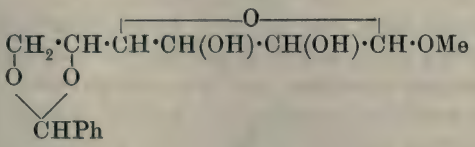
### *Constitution of Dimethyl Glucose.*

Considerable difficulty was experienced in determining the constitution of the sugar, as there are six possible isomeric dimethyl glucoses possessing reducing properties, and each should exist in two stereoisomeric modifications. Experimental methods for determining the position of substituting groups in the sugar molecule are far from satisfactory, but the bulk of the evidence points to the following structure as the most probable:



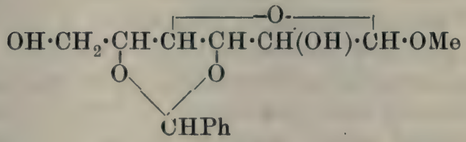
$$\mathrm{OH{\cdot}}\underset{\zeta}{\mathrm{CH_2}}\mathrm{{\cdot}}\underset{\epsilon}{\mathrm{CH(OH)}}\mathrm{{\cdot}}\overbrace{\underset{\delta}{\mathrm{CH}}\mathrm{{\cdot}}\underset{\gamma}{\mathrm{CH(OMe)}}\mathrm{{\cdot}}\underset{\beta}{\mathrm{CH(OMe)}}\mathrm{{\cdot}}\underset{\alpha}{\mathrm{CH}}}^{\mathrm{O}}\mathrm{{\cdot}OH}$$

As the compound is a reducing sugar and shows mutarotation, no methyl groups can be attached to the carbon atoms indexed α and δ. The sugar, moreover, formed no osazone, but a dimethyl glucosephenylhydrazone was produced under conditions favourable to osazone formation. One methyl group must therefore be attached in position β. The allocation of the remaining methyl group can only be arrived at indirectly by consideration of the possible structures for benzylidene methylglucoside. From the evidence quoted above, the possible formulæ for this substance are limited to three, of which the two most probable are the following:



$\mathrm{CH_2{\cdot}CH{\cdot}CH{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH{\cdot}OMe}$ ($\mathrm{CH_2}$ and CH joined through O, O to CHPh; O bridge to CH·OMe)

(I).



$\mathrm{OH{\cdot}CH_2{\cdot}CH{\cdot}CH{\cdot}CH{\cdot}CH(OH){\cdot}CH{\cdot}OMe}$

(II.)

The remaining possibility, in which the benzylidene residue couples the carbon atoms γ and ζ, may be reasonably left out of consideration, as it includes a seven-membered ring. Comparing the two structures shown above, it will be seen that the formation of a substance possessing formula II would not only involve the production of a six-membered ring, but the condensation of the benzaldehyde would in such case take place with hydroxyl groups situated in the *trans*-position with reference to the plane of the γ-oxidic ring.* Arguments have already been given (T., 1910, **97**, 1277) to show that this stereochemical arrangement results in considerable molecular strain, and is unlikely to occur when more stable positions are available for condensation. On the other hand, the hydroxyl groups attached to the carbon atoms ε and ζ are in the most favourable position for ring formation, and consequently we have selected formula I as the most suitable. This conclusion receives strong support from the following considerations. In methylglucoside, methylmannoside, and methylgalactoside, the same number of hydroxyl groups are in each case available for condensation with benzaldehyde, but their stereochemical arrangement is different:

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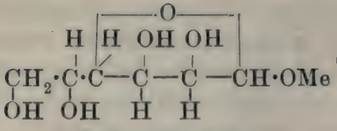
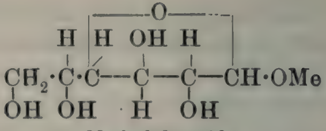
* See footnote to title of preceding paper, p. 564.



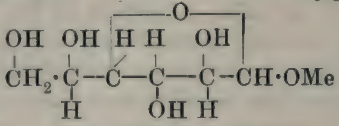
$\underset{OH}{CH_2}\cdot\overset{H}{\underset{OH}{C}}\cdot\overset{H}{C}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CH\cdot OMe$

Methylmannoside.



$\underset{OH}{CH_2}\cdot\overset{H}{\underset{OH}{C}}\cdot\overset{H}{C}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-CH\cdot OMe$

Methylglucoside.



$\overset{OH}{CH_2}\cdot\overset{OH}{\underset{H}{C}}-\overset{H}{C}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-CH\cdot OMe$

Methylgalactoside.

In methylmannoside, the pairs of hydroxyl groups attached to the carbon atoms β, γ, and ε, ζ, are in the most suitable position for ring formation admitted by the configuration. In methylglucoside and methylgalactoside, this is only true of the pair ε, ζ. It can scarcely be a mere coincidence that methylmannoside readily forms both a mono- and a di-benzylidene compound, whilst methylglucoside and methylgalactoside, irrespective of the conditions of the reaction, give only monobenzylidene derivatives

We thus conclude that in benzylidene methylglucoside, positions ε and ζ are protected from methylation, and that the methyl groups in dimethyl glucose occupy positions β and γ. This structure is in strict agreement with all the properties of the sugar, including its behaviour towards phenylhydrazine. The above considerations, which indicate that the condensation reactions of all the hydroxyl groups in sugars and glucosides are controlled by stereochemical arrangement, are capable of considerable application, and work in this direction is being continued.

## EXPERIMENTAL.

### *Preparation of* εζ-l-*Benzylidene* α-*Methylglucoside.*

Methylglucoside was condensed with benzaldehyde by the process described by Alberda van Ekenstein (*loc. cit.*). It is, however, quite unnecessary to use sodium sulphate in the reaction, or to take any other precaution to remove the water formed in the condensation; the benzaldehyde used should be very carefully fractionated. The best yields were obtained when the glucoside (50 grams) was finely powdered and sifted through muslin, mixed with a large excess of the aldehyde (300 c.c.), and heated for three hours at 145°. Thereafter, the temperature was maintained at 160° for nine hours. The product was precipitated by the addition of light petroleum, and crystallised from hot water. Yield = 25 per cent. of the glucoside used.

### *Isolation of* εζ-d-*Benzylidene* α-*Methylglucoside.*

In the course of several consecutive preparations of benzylidene methylglucoside, the crude product was precipitated as usual by the addition of light petroleum to the solution in benzaldehyde. The united mother liquors were put aside for several hours, when a small second crop of crystals was gradually deposited. On recrystallising this product from hot water, it was at once seen that the material did not consist of Alberda van Ekenstein's compound, as the latter separates in long, flexible needles, which form on the surface of the solution. In this case, the product crystallised on the bottom of the basin in small, warty aggregates of stout prisms, which were analysed after a second crystallisation:

Found, C = 59·35; H = 6·54; OMe = 11·6.

$C_{13}H_{15}O_5(OMe)$ requires C = 59·55; H = 6·38; OMe = 11·0 per cent.

The constants of the two isomerides are compared below:

| Alberda van Ekenstein's Compound. | New Isomeride. |
|---|---|
| *l*-Benzylidene α-Methyl-*d*-glucoside. | *d*-Benzylidene α-Methyl-*d*-glucoside. |
| M. p. 161—162° | 148—149° |
| $[\alpha]_D^{50°}$ + 85·0° | + 96·01° |
| Crystalline form: needles. | prisms. |
| Less soluble form. | More soluble form. |

### *Methylation of* l-*Benzylidene* α-*Methylglucoside.*

The material used in the alkylation was the isomeride melting at 161—162°. A solution of 30 grams of the benzylidene compound (1 mol.), in 80 c.c. of acetone, was mixed with 150 grams of methyl iodide (10 mols.), and 123 grams of silver oxide (5 mols.) were gradually added. The reaction was completed by heating on a water-bath for six hours. Next morning, large crystals of the product, measuring several centimetres, were found imbedded in the silver iodide. These were readily soluble in boiling acetone, and crystallised from the solution on concentration and cooling. After recrystallisation from light petroleum, the pure compound weighed 32·5 grams, so that the yield was practically quantitative:

Found, C = 61·93; H = 7·21; OMe = 28·2.

$C_{13}H_{13}O_3(OMe)_3$ requires C = 61·93; H = 7·10; OMe = 30·0 per cent.

εζ-*Benzylidene* βγ-*dimethyl* α-*methylglucoside* crystallises in prisms, melting at 122—123°. It is very sparingly soluble in water, but is readily dissolved by organic solvents.

Solvent: acetone; $c = 1·640$; $[\alpha]_D^{20°}$ + 97·03°.

### *Partial Hydrolysis of Benzylidene Dimethyl Methylglucoside.*

A 10 per cent. solution of the above compound in 1 per cent. aqueous hydrochloric acid was heated, with frequent shaking, at 95° for one hour. The reaction was conducted under a condenser, through which a current of carbon dioxide was passed. The benzaldehyde formed was removed by extraction with ether, the aqueous liquor neutralised with barium carbonate, and the filtrate evaporated to dryness at 45°/15 mm. The residue was then extracted with acetone, and the filtrate concentrated to a syrup, which solidified on cooling. Purification of the crude product was effected by several recrystallisations from benzene, a large excess of the solvent being employed. During the purification, an oil separated in the first instance from the dilute benzene solution; this was allowed to settle, after which the decanted solution was concentrated to the crystallising point. Throughout these operations moisture must be rigidly excluded until all hygroscopic by-products have been eliminated. Thirteen grams of pure dimethyl methylglucoside, melting at 80—82°, were thus obtained from 20 grams of benzylidene dimethyl methylglucoside:

Found: C=48·46; H=8·26; OMe=39·8.

$C_6H_9O_3(OMe)_3$ requires C=48·65; H=8·11; OMe=41·9 per cent.

$\beta\gamma$-Dimethyl $\alpha$-methylglucoside is readily soluble in water and organic solvents generally, sparingly so in ether or benzene, insoluble in hydrocarbon solvents. The compound reduced Fehling's solution only after hydrolysis, and displayed no mutarotation in solution:

| Solvent. | $c$. | $l$. | $\alpha^{20°}$. | $[\alpha]_D^{20°}$. |
|---|---|---|---|---|
| Water............ | 5·08 | 1 | +7·25 | +142·64° |
| Ethyl alcohol.. | 5·07 | 1 | 7·26 | 143·08 |
| Acetone ......... | 4·25 | 2 | 12·21 | 143·49 |

### *Hydrolysis of $\beta\gamma$-Dimethyl $\alpha$-Methylglucoside.*

The conversion into dimethyl glucose was carried out by boiling a solution of dimethyl methylglucoside, in 10 per cent. hydrochloric acid, for twenty minutes under a condenser. During the hydrolysis, the specific rotation altered from 142·4° to the constant value +58·5°, and recalculation of the latter figure for the concentration of dimethyl glucose formed on hydrolysis gives +62·4°. This agrees with the equilibrium value subsequently found for the sugar, so that the reaction is quantitative.

After removal of the acid with barium carbonate, evaporation to dryness at 45°/15 mm., extraction with boiling acetone and concentration, a syrup was obtained which gradually deposited a crop of minute prisms. The bulk of the sugar was, however, only obtained in the crystalline state after removal of the acetone and drying of the residue at 60°/15 mm. until constant in weight. Thereafter the compound was crystallised several times from dry ethyl acetate. Yield = 63 per cent. of the weight of glucoside used:

Found, C = 46·19; H = 7·83; OMe = 30·2.

$C_6H_{10}O_4(OMe)_2$ requires C = 46·15; H = 7·69; OMe = 29·8 per cent.

By the process described above, dimethyl glucose was obtained in the form of minute prisms readily soluble in water, the lower alcohols, and acetone, sparingly soluble in ethyl acetate, insoluble in ether or hydrocarbon solvents. The melting point observed was very indefinite (70—105°), and this behaviour was shown to be due to the presence of the stereoisomeric α- and β-forms.

### *βγ-Dimethyl β-Glucose.*

When the mixture of the α- and β-isomerides was crystallised from solutions in ethyl acetate containing from 10 to 20 per cent. of the solute, the sugar separated in brittle, warty aggregates. The initial specific rotations of successive crops varied from +29° to 58°, and the melting points similarly ranged from 80° to 104°. No separation of the two forms could thus be carried out.

On the other hand, crystallisation from a dilute solution in ethyl acetate (not more than 5 per cent.) gave a crop of pointed prisms which showed a tendency to arrange themselves in clusters. With a solution of intermediate concentration (about 7 per cent.), the crop consisted partly of the prisms referred to above, and partly of opaque, spherical aggregates, which were easily distinguished from the prismatic crystals, and could be mechanically separated from them.

The prisms proved to be the β-form of the sugar, and the spherical aggregates the α-isomeride, but only the former could be obtained in quantity by crystallisation from ethyl acetate. In preparing the material used in the rotations, the concentration of the solution was limited to 5 per cent., and the uniformity of each crystalline crop was confirmed by microscopic examination. The β-isomeride thus isolated was practically pure, but melted indefinitely at about 100°. The final purification consisted in preparing a 30 per cent. solution of the sugar in anhydrous alcohol, and precipitating the dissolved material in two crops by the addition of dry ether. The first portion to separate melted at 108—110°, and consisted of the pure β-form.

### *Mutarotation of βγ-Dimethyl β-Glucose.*

| Solvent. | $c$. | $l$. | Initial $\alpha^{20^\circ}$. | Final $\alpha$. | Initial $[\alpha]_D$. | Final $[\alpha]_D$. |
|---|---|---|---|---|---|---|
| Water............ | 5·00 | 1 | +0·53° → | +3·22° | +10·60 → | +64·4° |
| Alcohol ......... | 5·02 | 2 | 0·57 → | 4·96 | 5·68 → | 49·41 |
| Acetone ......... | 3·84 | 2 | 0·50 → | 3·91 | 6·52 → | 50·9 |

The speed with which equilibrium was attained in the three solvents differed in a marked degree. Thus, the aqueous solution assumed a constant rotation in about six hours. On the other hand, in alcoholic solution the change was exceedingly slow, while in acetone the sugar showed suspended mutarotation. In one experiment, in which anhydrous acetone, freshly prepared from the bisulphite compound, was used as a solvent, the alteration in specific rotation observed in fifteen days was only +6·5° → +8·2°. The permanent value of +49° was, however, reached in a few minutes on the addition of a catalyst. In each case, the curves representing the rotation changes were plotted, and, by extrapolation, the following initial values were indicated:

| Solvent. | Water. | Alcohol. | Acetone. |
|---|---|---|---|
| $[\alpha]_D^{20^\circ}$ | +5·7° | +5·68° | +5·9° |

In the case of the alcoholic and acetone solutions, these values are, of course, very little removed from those determined experimentally.

### *βγ-Dimethyl α-Glucose.*

Nuclei of dimethyl α-glucose were obtained, as described, by crystallisation of the equilibrium mixture of the sugar from 7 per cent. solutions in ethyl acetate. These nuclei proved of service in the following preparation of the α-form of the sugar. A 30 per cent. solution of dimethyl β-glucose in ethyl alcohol was heated at 100° for thirty minutes so as to establish equilibrium. Sufficient dry ether was then added to precipitate about one-half of the dissolved material in the first crop. This fraction was essentially the pure β-form. The filtrate was further diluted with ether, nucleated with the α-isomeride, and preserved in a freezing mixture for two days, when a second crop, consisting of the α-form, gradually separated. A third crop, which on microscopic examination appeared to be free from the prismatic β-form, was obtained on similarly nucleating the mother liquor.

βγ-Dimethyl α-glucose crystallises in dense spherical aggregates, which are quite opaque, so that no exact description of the crystalline form can be given. The crystals melted at 85—87°, and the compound showed downward mutarotation. Owing to the laborious nature of the separation of this isomeride, very little pure material was obtained, and the mutarotation was only determined in acetone solution, so as to obtain an accurate value for the initial point. The change thus observed, for $c=1$, was $+81·93° \dashrightarrow 48·3°$.

### *Proportion of α- and β-Forms present in Equilibrium in Solution.*

The necessary data for the above calculation are only available where acetone was used as the solvent.

$$\left.\begin{array}{l}\text{Initial } [\alpha]_D \text{ for } \alpha\text{-form} = +81·93° \\ \quad ,, \qquad ,, \qquad \beta \text{ form} = +\ 5·90°\end{array}\right\} \text{ Equilibrium } [\alpha]_D + 50·9°.$$

From these results, it will be seen that the equilibrium mixture contains 59 per cent. of the α-form and 41 per cent. of the β-isomeride. Owing to lack of material, the rotation of the α-form was not taken in aqueous solution, but it may be reasonably assumed that it does not differ notably from the value found in acetone solution. This is justified by the practical coincidence of the initial specific rotations of the β-form in these solvents, as determined by extrapolation. Further, the activity of dimethyl methylglucoside, which is an α-form, is likewise unaffected by the nature of the solvent. The data for the calculation thus becomes:

$$\left.\begin{array}{l}\text{Initial } [\alpha]_D \text{ for } \alpha\text{-form} = +81·93° \\ \quad ,, \qquad ,, \qquad \beta\text{-form} = +\ 5·7°\end{array}\right\} \text{ Equilibrium } [\alpha]_D = +64·4°.$$

This corresponds with a mixture consisting of 77 per cent. of the α-form and 23 per cent. of the β-modification, values which are widely different from those found in the case of glucose.

### *Effect of Heat in Altering the Equilibrium.*

On recovering the sugar from an aqueous solution, which had attained equilibrium, by evaporation of the solvent at 30°/12 mm., the product showed practically no mutarotation. The equilibrium thus appears to be only slightly affected by change of concentration. A specimen of the sugar, isolated in the manner described above, was kept in the fused condition at 120° for an hour, after which, on dissolving the product in water, extensive upward mutarotation was observed. This treatment is known to alter equilibria in methylated sugars in the direction $\alpha \rightleftarrows \beta$, and the result thus justifies the stereochemical nomenclature we have applied to the two forms of this sugar.

### *βγ-Dimethyl Glucosephenylhydrazone.*

Several attempts were made to prepare an osazone from dimethyl glucose, but, although the process was modified in various ways, no sparingly soluble product was obtained, and the sugar was resinified.

Condensation with phenylhydrazine was, however, effected under the following conditions. A solution of the sugar (1 mol.), in an equal weight of water, was mixed with phenylhydrazine (3 mols.), and after thorough mixing, the liquid was preserved in the dark for six weeks in a sealed tube. A homogeneous syrup was thus obtained, which was dissolved in ether, the solution shaken successively with dilute acetic acid and water, dried over sodium sulphate, and evaporated. This treatment removed excess of the base, together with any free sugar. The product was a pale yellow syrup, which crystallised completely on keeping. No suitable recrystallising medium could be found, and the compound, which possessed the usual properties of a hydrazone, was analysed after heating gently in a vacuum until constant in weight:

Found, N = 9·80.

$C_{14}H_{22}O_5N_2$ requires N = 9·40 per cent.

This nitrogen content is in itself sufficient proof that the compound is a hydrazone, and not an osazone. In a duplicate experiment, in which glucose was used, the sugar was completely converted into glucosephenylosazone.

Part of the expense of the foregoing investigations was defrayed by annual research grants received from the Carnegie Trust, for which the authors desire to express their indebtedness.

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UNIVERSITY OF ST. ANDREWS.

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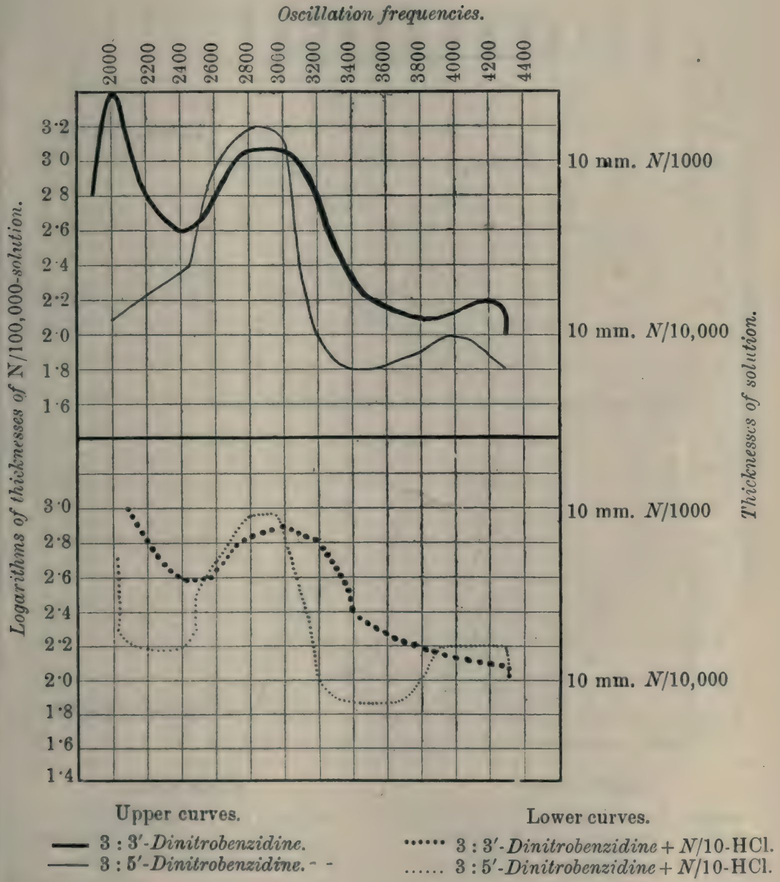
## LXVI.—*Studies in the Diphenyl Series. Part IV. The Absorption Spectra of the Two Isomeric* o-*Dinitrobenzidines.*

By JOHN CANNELL CAIN, ALEXANDER KILLEN MACBETH, and ALFRED WALTER STEWART.

IN a previous communication by one of us in conjunction with Coulthard and Miss Micklethwait (T., 1912, **101**, 2298) it was shown that *o*-dinitrobenzidine exists in two isomeric forms, one being scarlet and melting at 275°, whilst the other is bright red and melts at 233°. In view of the interesting nature of this isomerism, it seemed of importance to bring all possible evidence to bear upon the point; and in the present communication the description is given of the absorption spectra of the two compounds. For the sake of convenience in reference, we have adhered to the previous nomenclature, and describe the compounds as 3 : 3′-dinitrobenzidine and 3 : 5′-dinitrobenzidine respectively.

The absorption spectra of the two substances in alcohol are shown in the upper curves of Fig. 1. It will be seen that in the ultra-violet region the graphs resemble each other to a certain extent, both having a band in the region $^1/\lambda$ 3100—3800. In the visible part of the spectrum the two curves differ considerably from one another, as in the curve for the 3 : 3′-compound there is a complete band the head of which lies about $^1/\lambda$ 2400, whilst the graph for the 3 : 5′-compound shows the presence of a much deeper band, the

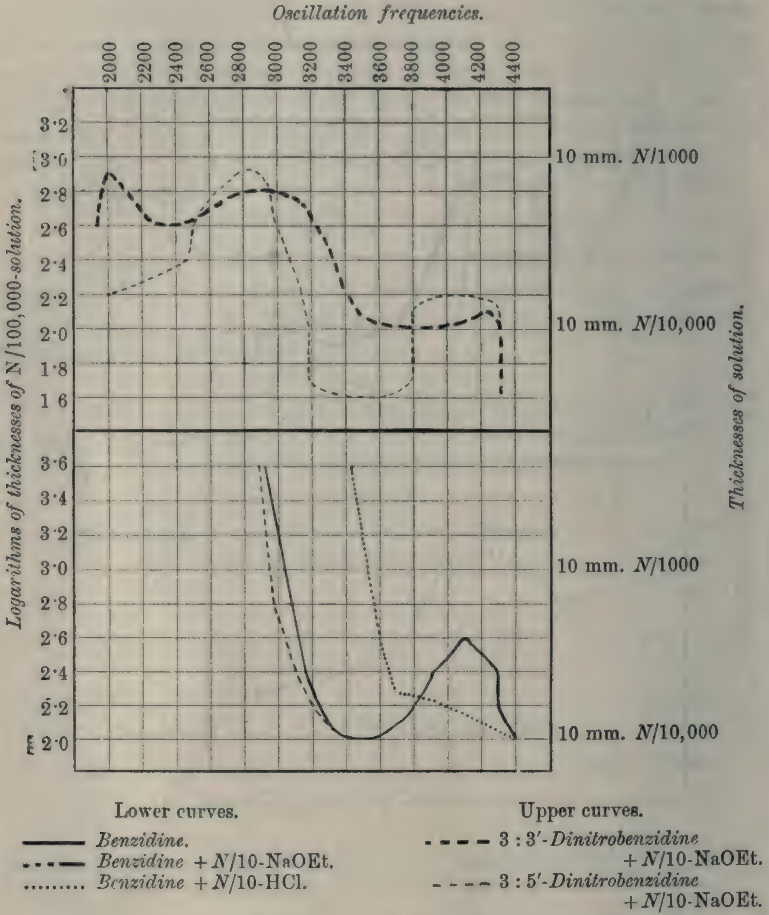
Fig. 1.



lower limit of which lies outside the region of our photographs. The curve for the 3 : 3′-compound also has a band the other side of which we were unable to reach.

This marked difference between the two graphs as a whole shows that the distribution of affinity cannot be precisely the same in

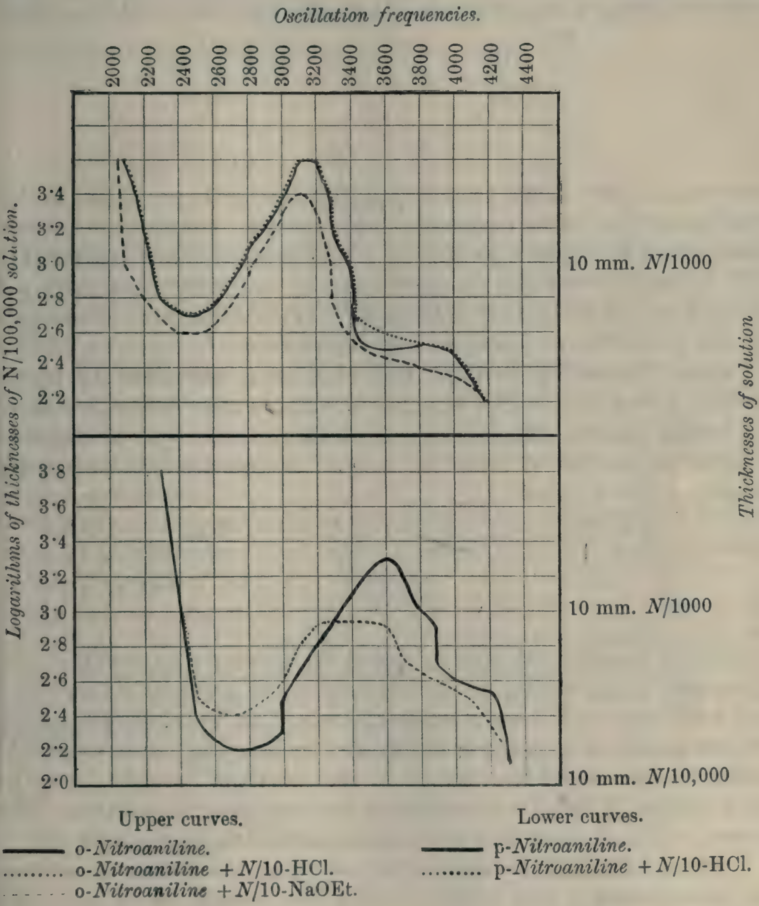
FIG. 2.



both compounds, and it is therefore necessary to examine more closely the various groups which make up the molecule in each case.

The compound which is most closely allied in structure to the dinitrobenzidines is *o*-nitroaniline, and we therefore photographed its spectrum in alcoholic solution,* and also in the presence of excess of hydrochloric acid and sodium ethoxide. The resulting graphs are shown in Fig. 3. A comparison of the curve of the pure substance with those of the dinitrobenzidines shows that there is a general resemblance between *o*-nitroaniline and the 3 : 3′-compound; but that the 3 : 5′-derivative differs from *o*-nitroaniline in the region $^1/\lambda$ 2000—2800, and also has a well-marked band at $^1/\lambda$ 3100—4000, where only a very shallow depression is shown in the *o*-nitroaniline spectrum. It is clear that if we can gain some

FIG. 3.



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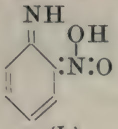
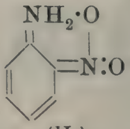
* This had already been done by Morgan, Jobling, and Barnett (T., 1912, **101**, 1213), the results being similar to ours.

insight into the structure of the *o*-nitroaniline molecule it will aid us in our further consideration of the dinitrobenzidines, and this question must therefore now be considered.

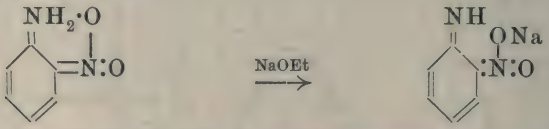
An examination of the spectrum of *o*-nitroaniline shows that it has a band similar to those contained in the spectra of some quinones; and we are therefore justified in assuming that there is a quinonoid grouping in the *o*-nitroaniline molecule. This would lead us to assign the structure (I) to *o*-nitroaniline. At this point,


(I.)


(II.)

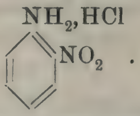
however, a new factor comes in; for the nitro-group is in the *aci*-form within active range of a basic radicle. Interaction between these would take place, producing a substance of the structure (II). This formula resembles in some respects one which has been put forward by Meldola and Hollely (T., 1912, **101**, 918) to account for the properties of picramic acid derivatives.

Before proceeding further, this idea must be tested so far as possible to see if it can be brought into agreement with other facts. By adding sodium ethoxide to a substance of this type it might be possible to convert it into the salt of a pseudo-acid having the structure shown below:



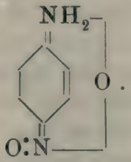
Now in order to do this it would be necessary to break a five-membered ring, which, as is well known, is a fairly stable type; and when this was done a substance would be obtained the quinonoid structure of which was unchanged in essential; thus we should expect to find very little change in the spectrum brought about by the addition of sodium ethoxide to the nitroaniline solution. The curves in Fig. 3 show that the experimental data agree with this.

A second test can be applied by studying the action of acid on the nitroaniline. The action in this case would be to open the ring and cause the substance to revert to the benzenoid form, an ordinary salt of the ammonium type being formed:



Examination of the curves shows that this does not take place.

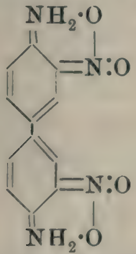
The substance retains its quinonoid character even in the presence of excess of acid. How can this be explained? We have already pointed out that the five-membered ring is a very stable type, and it seems likely that the action of the acid may not be sufficient to rupture it. In order to test this idea it is only necessary to substitute a less stable ring for the five-membered one; and a case in point is *p*-nitroaniline. Here the pure substance shows a band similar to that of *o*-nitroaniline, although much broader; so that the structure may be similarly written:



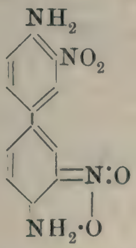
Now this internal salt contains a seven-membered ring instead of the five-membered one of *o*-nitroaniline; and such a seven-membered ring would, on general grounds, be less stable than the five-membered one. It will therefore be more easily ruptured by the action of acid, and the compound would tend to revert to the benzenoid structure to some extent and showing a less marked quinonoid band. The lower curves in Fig. 3 show that this holds good, for in this case the band obviously decreases in persistence in presence of acid.

This evidence justifies us in assuming that *o*-nitroaniline has the internal salt structure, and that, further, this ring is fairly stable in the presence of acid.

Let us now look at the benzidine derivatives in the light of this hypothesis. In their case we have to explain the occurrence of the substance in two isomeric forms, one of which is more closely allied to *o*-nitroaniline than the other. The formulæ below give one possible explanation of the difference:



3 : 3′-Dinitrobenzidine.



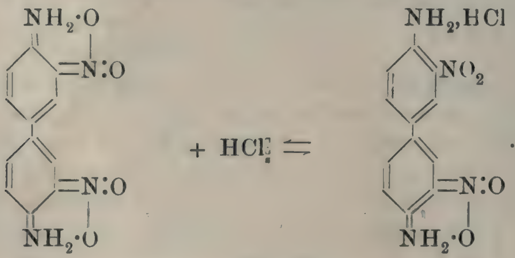
3 : 5′-Dinitrobenzidine.

In the one formula both benzene nuclei are in the quinonoid form, whilst in the second there is one benzenoid and one quinonoid nucleus.

We must now apply a further series of tests to these formulæ with the object of finding out whether they meet fresh requirements.

We have seen that in *o*-nitroaniline the five-membered ring is stable, to a great extent, in the presence of acid. From this we deduce that when acid is added to a solution of the diquinonoid benzidine derivative there would not be a marked change in the spectrum. A comparison of the curves in Fig. 1 will show that this corresponds with the experimental result; very little change in general character takes place when acid is added to the solution. On the other hand, in the case of the benzenoid-quinonoid compound there is a free amino-group which should unite with this acid and become saturated, thus giving a reversion towards the benzene spectrum. Let us take benzidine* as a comparison substance. As can be seen from the lower curves in Fig. 2, the addition of hydrochloric acid to benzidine has the effect of shutting up the band and replacing it by a rapid extension of the spectrum. An examination of the curves of 3:5′-dinitrobenzidine alone and with hydrochloric acid present (Fig. 1) shows that a similar closing of the band takes place, although it is not so complete as in the case of benzidine, probably owing to the presence of the second nucleus in the quinonoid condition, which will be a disturbing factor; thus the hypothesis fits the facts very closely.

Attention should be drawn to the fact that hydrochloric acid is not quite without action in the case of 3:3′-dinitrobenzidine, although the alteration in the spectrum in this region is slight. The change may be ascribed to the tendency toward equilibrium between the two forms; in the presence of excess of acid a small amount of the ring compound would naturally tend to revert even in this case to the benzenoid type; but as can be seen from the curves, the amount of change which takes place is evidently very small:



Thus, from the spectroscopic point of view these formulæ form a basis on which to explain the isomerism of the two *o*-dinitro-compounds, and the existence of two *o*-dinitrodiphenyls, and of the acetyl derivatives of the *o*-dinitrobenzidines, can be accounted for in a similar way, thus:

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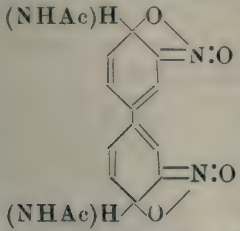
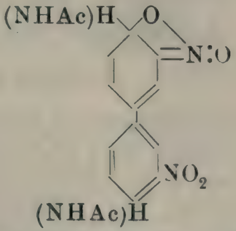
* Benzidine shows a slight deviation from Beer's law between *N*/10,000- and *N*/100,000-solutions. For the sake of simplicity, only the *N*/10,000-curve is given.



and



It must be frankly stated, however, that spectroscopic evidence alone is not sufficient to decide a purely chemical question unless it is well supported by purely chemical data. In the present case the chemical evidence appears to favour the view put forward above, as it tends to show that the amino-groups are not perfectly normal in behaviour; for instance, the compounds do not readily form hydrochlorides as they would do if the amino-groups were free to react with acid, like the corresponding groups in benzidine.

The chief objection which can be brought against these formulæ is that it is difficult to understand why one form should not pass into the other; thus no change of either form is effected by treatment with sodium ethoxide. The stability of the five-membered ring when once formed would explain the non-conversion of the 3 : 3′-compound into its isomeride; whilst it is well known that there is little inclination for benzenoid substances to revert to the quinonoid type, which would cover the case of the stability of the 3 : 5′-substance.

### *Conclusions.*

(1) The spectra of the two *o*-dinitrobenzidines show that there is a marked difference between the two substances.

(2) There is a resemblance in a certain degree between the spectrum of *o*-nitroaniline and that of 3 : 3′-dinitrobenzidine.

(3) From the results obtained by studying the spectra of the *o*-dinitrobenzidines in the presence of acid and alkali, it appears probable that they differ from each other in the constitution of their benzene nuclei, the one compound containing two quinonoid rings, whilst the other is made up of a benzenoid and a quinonoid nucleus.

The Chemical Department,
The Queen's University of Belfast.

# LXVII.—*The Influence of the Constitution of Tertiary Bases on the Rate of Formation of Quaternary Ammonium Salts. Part I.*

By Ebenezer Rees Thomas.

The investigations of Hofmann, Menschutkin, Bischoff, Wedekind, and others, have shown that the constitution of organic bases exercises a profound influence on their reactions with halogen compounds, but notwithstanding the attention which has been bestowed on the kinetics of these reactions, the velocity-constant measurements have dealt almost entirely with the effect of the constitution of the haloid on the course of the reaction.

N. Menschutkin (*Zeitsch. physikal. Chem.*, 1890, **5**, 589; **6**, 41; 1895, **17**, 193; 1900, **34**, 157; *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 46; 1902, **34**, 411; *Ber.*, 1895, **28**, 1398; 1897, **30**, 2775, 2966; 1905, **38**, 2465) has, however, carried out a complete investigation of a number of reactions of this type, studying not only the influence of the constitutions of both reagents, but also that of the solvent on the rate of reaction. In his work on the effect of the constitution of the base he dealt mainly with primary and secondary amines. The results which he obtained as to the influence of the constitution of tertiary bases will find further mention in this paper. Moore, Somervell, and Derry (T., 1912, **101**, 2459) show that some of Menschutkin's results are open to criticism on theoretical grounds. It is suggested that the experimental method described in the present communication might be expected to yield results of a higher degree of accuracy than those obtained by the method used by Menschutkin.

The velocity constants for the reaction between various aromatic tertiary bases and allyl bromide in $N/10$-absolute alcohol solution at 40·0° were determined. In some cases the constant for benzyl bromide was also measured.

It was found that with some compounds accurate results could only be obtained when the amount of quaternary ammonium bromide was estimated gravimetrically as silver bromide. This rendered the study of the very early stages of the reaction impracticable; but as in nearly every case the value of the constant remains the same over widely different periods, this is not of much consequence so far as the comparison of the rates is concerned. It was also found necessary to remove the unaltered haloid before precipitating the silver bromide, and this was done in every experiment. The latter precaution, if unnecessary for slowly reacting haloids, certainly cannot be neglected in the case of allyl bromide.

Wedekind (*Ber.*, 1899, **32**, 511; *Annalen*, 1901, **318**, 90) has extended the investigations in this field by studying the influence of the constitution of certain tertiary bases on quaternary ammonium salt formation. He determined the amount of salt formed at the end of a certain period of time under certain conditions, the estimation in each case being made by weighing the washed and dried product of the reaction.

It was considered advisable to carry out a systematic investigation of the actual velocity constants for various aromatic tertiary bases, under the conditions already described, in the hope that an exact measure might be made of the influence of the nature and position of the groups attached to the nitrogen atom.

The following results were obtained:

| | Velocity constants | | Ratio, |
|---|---|---|---|
| | Allyl bromide. | Benzyl bromide. | $\frac{\text{Benzyl}}{\text{allyl.}}$ |
| Dimethylaniline | 1·08 | 6·34 | 6·0 |
| Methylethylaniline | 0·71 | | |
| Diethylaniline | 0·094 | | |
| Methylpropylaniline | 0·48 | | |
| Methylallylaniline | 0·350 | | |
| Benzylmethylaniline | 0·123 | | |
| Methylacetanilide | 0·032 | 0·134 | 4·1 |
| Benzylideneaniline | 0·8 | | |
| Dimethyl-*o*-toluidine | 0·057 | 0·235 | 4·1 |
| Dimethyl-*m*-toluidine | 1·54 | | |
| Dimethyl-*p*-toluidine | 2·80 | | |
| *p*-Bromodimethylaniline | 0·284 | 1·93 | 6·8 |
| Dimethyl-*p*-aminobenzaldehyde | 0·04 | | |
| Pyridine | 0·43 | | |
| Quinoline | 0·063 | | |
| *iso*Quinoline | 0·485 | | |
| Methyltetrahydroquinoline | 0·413 | | |
| Ethyltetrahydroquinaldine | 0·037 | | |
| 2-Methylquinoline (quinaldine) | 0·035 | | |
| Methyltetrahydroquinaldine | 0·084 | | |
| Acetylpiperidine | 0·030 | 0·136 | 4·5 |

## EXPERIMENTAL.

### *Purification of Materials.*

The alcohol was purified by boiling rectified spirit over lime under a reflux condenser until all the lime was broken up, and subsequent distillation. This operation was repeated, and the alcohol then treated twice in a similar way with 1 per cent. of freshly turned calcium. The purity was finally tested by means of a velocity-constant determination. Rough preliminary experiments were generally carried out in rectified spirit solution, and it was found that the presence of water in the alcohol tends to accelerate the rate of reaction.

Pure allyl bromide was redistilled and kept in a desiccator protected from light.

It was distilled in small quantities as required, in order to obviate long keeping, whilst the velocity constant for each specimen was determined with a standard substance. In the case of one specimen of allyl bromide which was found to give rather low results, the rates for three standard bases were determined, and it was found that the ratio of the constants for the standard bromide to the constants for this bromide were 1·08, 1·07, 1·09 for methylallylaniline, *iso*quinoline, and methylethylaniline respectively (compare experiments 2 and 5). The constants for the bases which have been measured with this specimen of allyl bromide (called K′) have therefore been multiplied by 1·08, so that all the numbers are strictly comparable.

The solid bases were ali purified by recrystallisation, and in nearly every case of a liquid base a crystalline derivative was prepared and purified, from which the base was subsequently recovered. The quality of the numbers obtained was in each case taken as the final test of purity, so that purification was carried out until a good constant was obtained.

### *Method.*

The reactions were carried out at 40° in glass-stoppered bottles, which were, as far as possible, protected from the action of light. Since only the comparative values of the constants are of importance, it was found most convenient to refer all data to concentrations at 15°.

*N*/5-Solutions of the base and of allyl bromide were therefore made up at 15° and placed in the 40° thermostat, together with the reaction-vessel. When the solutions (now a little less than *N*/5) had attained the temperature of the bath, equal quantities of the two solutions were in turn transferred to the reaction vessel by means of a pipette, the bottle being well shaken and the exact time of mixing noted.

At definite intervals of time, about 20 c.c.* of the reaction mixture were transferred to a small separating funnel containing about 70 c.c. of about *N*/10- to *N*/20-nitric acid (which at once arrested the reaction), and about 40 c.c. of light petroleum. After shaking and settling, nearly all the light petroleum was syphoned off, a second quantity of 30 c.c. being then added in order to remove any remaining traces of allyl bromide.

The aqueous layer was transferred to a small beaker, the light petroleum was washed twice with small quantities of water, and the washings were added to the solution in the beaker. Silver nitrate solution was then added; the resulting precipitate was coagulated by stirring, and then collected, washed, dried, and weighed.

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* The pipettes wer calibrated so that the volume at 15° of the solution which hey delivered at 40° was known.

The results* given below were calculated according to the usual formula for a bimolecular reaction:

$$K = \frac{1}{t}\frac{x}{a(a-x)},$$

$a$ and $x$ being expressed as the number of gram-molecules per litre at 15°.

Column I gives time in hours elapsed since time of mixing; II, actual weight of silver bromide obtained; III, $x$ calculated from II; IV, value of constant $K$. (As the maximum amount of iodide would give a decinormal solution, the numbers obtained by multiplying those in column III by 1000 express the percentage of salt formed.)

### *Experiments with Allyl Bromide.*

### 1. *Dimethylaniline.*

| *A.* | I. | II. | III. | IV. |
|---|---|---|---|---|
| | 4·5 | 0·1180 | 0·03235 | 1·06 |
| | 5·5 | 0·1355 | 0·03715 | 1·07 |
| | 7·5 | 0·1628 | 0·04461 | 1·07 |
| | 8·8 | 0·1785 | 0·04893 | 1·09 |
| | 10·67 | 0·1975 | 0·05415 | 1·10 |

Mean $K$ of $A = 1·08$. Mean $K$ of $B = 1·085$.

Mean of $A$ and $B = 1·08$.

### 2. (*a*) *Methylethylaniline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 2·78 | 0·0570 | 0·0156 | 0·667 |
| 4·53 | 0·0843 | 0·0231 | 0·663 |
| 5·95 | 0·1017 | 0·0279 | 0·650 |
| 6·63 | 0·1115 | 0·03056 | 0·664 |
| 7·25 | 0·1178 | 0·0323 | 0·658 |

Mean $K'$ of $A = 0·660$.
Mean $K'$ of $B = 0·661$.

Mean of $A$ and $B = 0·6605$.

$K = 0·6605 \times 1·08 = 0·713$.

### 2. (*b*) *Methylethylaniline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 4·2 | 0·0850 | 0·0233 | 0·72 |
| 4·53 | 0·0900 | 0·0247 | 0·72 |
| 6·2 | 0·1130 | 0·0310 | 0·72 |

Mean $K = 0·72$.

Ratio $K/K' = 1·09$.

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* In most cases, two determinations (*A* and *B*) were made, and the results of one determination are given in full.

### 3. *Diethylaniline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 30·05 | 0·0790 | 0·02165 | 0·092 |
| 47·5 | 0·1091 | 0·0299 | 0·090 |
| 71·4 | 0·1450 | 0·03976 | 0·092 |
| 80·6 | 0·1580 | 0·04332 | 0·095 |
| 96·7 | 0·1765 | 0·0484 | 0·097 |

Mean $K$ of $A$ = 0·093.
Mean $K$ of $B$ = 0·0955.

Mean of $A$ and $B$ = 0·094.

### 4. *Methylpropylaniline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 7·92 | 0·1003 | 0·0275 | 0·479 |
| 9·42 | 0·1122 | 0·0308 | 0·472 |
| 11·0 | 0·1258 | 0·0345 | 0·479 |
| 13·53 | 0·1442 | 0·03955 | 0·483 |
| 21·07 | 0·1838 | 0·0504 | 0·482 |

Mean $K$ of $A$ = 0·479.
Mean $K$ of $B$ = 0·480.

Mean of $A$ and $B$ = 0·480.

### 5. (*a*) *Methylallylaniline* (K′).

| I. | II. | III. | IV. |
|---|---|---|---|
| 7·8 | 0·0735 | 0·0215 | 0·323 |
| 10·3 | 0·0920 | 0·0252 | 0·327 |
| 11·2 | 0·0977 | 0·0268 | 0·327 |
| 12·08 | 0·1040 | 0·0285 | 0·330 |

Mean $K'$ of $A$ = 0·327.
Mean $K'$ of $B$ = 0·322.

Mean $K'$ of $A$ and $B$ = 0·324.

Therefore mean $K = 0·324 \times 1·08$
$= 0·350$

### 5. (*b*) *Methylallylaniline* (K).

| I. | II. | III. | IV. |
|---|---|---|---|
| 9·05 | 0·0878 | 0·0241 | 0·350 |
| 10·4 | 0·0972 | 0·02665 | 0·351 |
| 11·4 | 0·1042 | 0·02855 | 0·351 |
| 12·7 | 0·1123 | 0·0308 | 0·350 |
| 13·73 | 0·1190 | 0·0326 | 0·352 |

Mean $K$ = 0·350.

Ratio: $K/K' = \dfrac{0·350}{0·324}$.
$= 1·08$.

### 6. *Methylbenzylaniline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 21·00 | 0·0747 | 0·0205 | 0·123 |
| 27·37 | 0·0912 | 0·0250 | 0·122 |
| 32·7 | 0·1040 | 0·0285 | 0·122 |
| 43·3 | 0·1278 | 0·03505 | 0·124 |
| 46·43 | 0·1337 | 0·03665 | 0·1246 |

Mean $K$ of $A$ = 0·123.
Mean $K$ of $B$ = 0·123.

Mean of $A$ and $B$ = 0·123.

### 7. *Methylacetanilide.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 65·3 | 0·0630 | 0·0173 | 0·0320 |
| 88·4 | 0·0808 | 0·02215 | 0·0322 |
| 134·9 | 0·1120 | 0·0307 | 0·0328 |

Mean $K$ of $A$ = 0·0323.
Mean $K$ of $B$ = 0·0322.
Mean $K$ of $C$ = 0·0314.

Mean of $A$, $B$ and $C$ = 0·032.

### 8. *Benzylideneaniline.*

| I | II. | III. | IV. |
|---|---|---|---|
| 2·3 | 0·0697 | 0·0191 | 0·835 |
| 3·83 | 0·0870 | 0·02385 | 0·818 |
| 4·7 | 0·0988 | 0·0271 | 0·791 |
| 5·27 | 0·1062 | 0·0292 | 0·781 |

Mean ($K$ ?) = 0·8.

### 9. *Dimethyl*-o-*toluidine.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 47·66 | 0·0773 | 0·0212 | 0·0564 |
| 65·2 | 0·0960 | 0·02632 | 0·0548 |
| 95·5 | 0·1287 | 0·0353 | 0·0571 |
| 115·4 | 0·1488 | 0·0408 | 0·0597 |

Mean $K$ of $A$ = 0·057.
Mean $K$ of $B$ = 0·057.

Mean of $A$ and $B$ = 0·057.

### 10. *Dimethyl*-m-*toluidine.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 2·47 | 0·0944 | 0·0259 | 1·41 |
| 3·72 | 0·1267 | 0·03475 | 1·43 |
| 4·82 | 0·1475 | 0·04045 | 1·41 |

Mean $K'$ of $A$ = 1·42.
Mean $K'$ of $B$ = 1·43.

Mean $K'$ of $A$ and $B$ = 1·425.

Therefore $K = 1·425 \times 108$.
$= 1·54$.

### 11. *Dimethyl*-p-*toluidine.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 1·27 | 0·0992 | 0·0265 | 2·84 |
| 1·92 | 0·1304 | 0·0348 | 2·79 |
| 2·5 | 0·1538 | 0·0411 | 2·79 |
| 3·0 | 0·1710 | 0·0456 | 2·80 |
| 3·28 | 0·1788 | 0·0477 | 2·81 |

Mean $K$ of $A$ = 2·80.
Mean $K$ of $B$ = 2·80.
Mean of $A$ and $B$ = 2·80.

### 12. p-*Bromodimethylaniline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 9·45 | 0·0810 | 0·0222 | 0·302 |
| 12·78 | 0·1010 | 0·0277 | 0·300 |
| 16·60 | 0·1184 | 0·0325 | 0·290 |
| 19·66 | 0·1280 | 0·0351 | 0·275 |
| 22·79 | 0·1375 | 0·0377 | 0·266 |

Mean $K$ of $A$=0·286.
Mean $K$ of $B$=0·282.

Mean of $A$ and $B$=0·284.

### 13. p-*Dimethylaminobenzaldehyde.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 67·8 | 0·0852 | 0·02335 | 0·0450 |
| 87·6 | 0·1040 | 0·0285 | 0·0455 |
| 91·4 | 0·1078 | 0·0296 | 0·0460 |

Mean $K$=0·0455.

### 14. *Pyridine.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 9·92 | 0·1020 | 0·0280 | 0·392 |
| 12·35 | 0·1193 | 0·0327 | 0·394 |
| 13·95 | 0·1308 | 0·03585 | 0·401 |
| 15·66 | 0·1423 | 0·0390 | 0·408 |
| 18·17 | 0·1548 | 0·04245 | 0·406 |

Mean $K'$=0·400.

$K$=0·400 × 1·08.
=0·43.

### 15. *Methyltetrahydroquinaldine.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 19·75 | 0·0526 | 0·0144 | 0·085 |
| 42·6 | 0·0960 | 0·0263 | 0·084 |
| 47·83 | 0·1035 | 0·0284 | 0·083 |
| 52·0 | 0·1098 | 0·0301 | 0·083 |

Mean $K$=0·084.

### 16. *Quinoline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 36·86 | 0·0638 | 0·0175 | 0·0574 |
| 60·81 | 0·0960 | 0·0263 | 0·0587 |
| 74·18 | 0·1094 | 0·0300 | 0·0578 |
| 85·14 | 0·1230 | 0·03372 | 0·0597 |

Mean $K'$ of $A$=0·0584.
Mean $K'$ of $B$=0·0584.

Mean $K'$ of $A$ and $B$=0·0584.

Therefore $K$=0·0584 × 1·08.
=0·063.

### 17. iso*Quinoline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 5·27 | 0·0692 | 0·01897 | 0·444 |
| 7·4 | 0·0913 | 0·02504 | 0·451 |
| 9·15 | 0·1055 | 0·02893 | 0·445 |
| 10·28 | 0·1150 | 0·03153 | 0·449 |

Mean $K'$ of $A$=0·447.
Mean $K'$ of $B$=0·451.

Mean $K'$ of $A$ and $B$=0·449.

Therefore $K$=0·449 × 1·08.
=0·485.

### 18. *Methyltetrahydroquinoline.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 11·1 | 0·1148 | 0·0315 | 0·414 |
| 15·0 | 0·1405 | 0·0385 | 0·417 |
| 18·27 | 0·1575 | 0·0432 | 0·416 |
| 20·51 | 0·1683 | 0·0461 | 0·417 |
| 23·25 | 0·1790 | 0·0491 | 0·415 |

Mean $K$ of $A$=0·416.
Mean $K$ of $B$=0·410.

Mean of $A$ and $B$=0·413.

### 19. *Ethyltetrahydroquinaldine.*

| I. | II. | III. | IV. |
|---|---|---|---|
| 42·2 | 0·0493 | 0·0135 | 0·0370 |
| 88·17 | 0·0900 | 0·0247 | 0·0372 |
| 94·5 | 0·0942 | 0·02583 | 0·0369 |
| 97·97 | 0·0972 | 0·02665 | 0·0371 |

Mean $K$=0·0370

### 20. 2-*Methylquinoline* (*Quinaldine*).

| I. | II. | III. | IV. |
|---|---|---|---|
| 70·96 | 0·0680 | 0·01865 | 0·0323 |
| 95·6 | 0·0857 | 0·0235 | 0·0322 |
| 119·72 | 0·1021 | 0·0280 | 0·0325 |

Mean $K'$ of $A$=0·0323.
Mean $K'$ of $B$=0·0325.

Mean $K'$ of $A$ and $B$=0·0324.

Therefore $K$=0·0324 × 1·08.
=0·0350.

### 21. *Acetylpiperidine*.

| I. | II. | III. | IV. |
|---|---|---|---|
| 67·0 | 0·0617 | 0·0169 | 0·0304 |
| 86·9 | 0·0760 | 0·0209 | 0·0303 |
| 89·73 | 0·0783 | 0·0215 | 0·0305 |

Mean $K$=0·0304.

## *Experiments with Benzyl Bromide.*

### 22. *Dimethylaniline*.

| I. | II. | III. | IV. |
|---|---|---|---|
| 0·741 | 0·1172 | 0·03214 | 6·39 |
| 0·991 | 0·1407 | 0·03856 | 6·33 |
| 1·241 | 0·1605 | 0·044 | 6·33 |
| 1·49 | 0·1770 | 0·04853 | 6·325 |

Mean $K$ of $A$=6·34.
Mean $K$ of $B$=6·35.

Mean of $A$ and $B$=6·34.

### 23. *Methylacetanilide*.

| I. | II. | III. | IV. |
|---|---|---|---|
| 15·68 | 0·0654 | 0·01745 | 0·132 |
| 20·43 | 0·0798 | 0·0213 | 0·132 |
| 25·68 | 0·0956 | 0·0255 | 0·133 |
| 27·33 | 0·1014 | 0·0271 | 0·136 |
| 36·5 | 0·1252 | 0·0334 | 0·137 |

Mean $K$=0·134.

### 24. *Dimethyl-o-toluidine*.

| I. | II. | III. | IV. |
|---|---|---|---|
| 12·5 | 0·0773 | 0·0212 | 0·215 |
| 15·6 | 0·0938 | 0·0257 | 0·222 |
| 21·65 | 0·1248 | 0·0342 | 0·241 |
| 35·0 | 0·1766 | 0·0484 | 0·268 |

Mean $K$ of $A$=0·24.
Mean $K$ of $B$=0·23.

Mean of $A$ and $B$=0·235.

A gradual rise in the constant is observed (compare Long, *loc. cit.*).

### 25. p-*Bromodimethylaniline*.

| I. | II. | III. | IV. |
|---|---|---|---|
| 2·38 | 0·1145 | 0·0314 | 1·92 |
| 3·08 | 0·1346 | 0·0369 | 1·90 |
| 3·65 | 0·1513 | 0·0415 | 1·94 |
| 4·52 | 0·1707 | 0·0468 | 1·95 |
| 5·21 | 0·1845 | 0·0506 | 1·96 |

Mean $K$=1·93.

### 26. *Acetylpiperidine*.

| I. | II. | III. | IV. |
|---|---|---|---|
| 21·92 | 0·0856 | 0·0229 | 0·135 |
| 25·75 | 0·0966 | 0·0258 | 0·135 |
| 29·58 | 0·1068 | 0·0285 | 0·135 |
| 32·75 | 0·1166 | 0·0311 | 0·138 |

Mean $K$ of $A$=0·136.
Mean $K$ of $B$=0·137.

Mean of $A$ and $B$=0·136.

It is hoped that further research on these lines may lead to exact general conclusions as to the mechanism of the reaction. At the present stage of the work perhaps the following points may be noted.

1. The reaction-velocities for some of these bases have been determined under different conditions by other workers; Menschutkin measured the rates with allyl bromide (*a*) and methyl bromide (*b*) at 100° in benzene solution; Long (T., 1911, **99**, 2164) used *iso*amyl alcohol as solvent, and determined the rates with *iso*amyl bromide at 92·6°. The following is a comparative table of the results, the constant for pyridine being taken as 100:

| | | Menschutkin. | | |
|---|---|---|---|---|
| | Long. | *a*. | *b*. | This paper. |
| *iso*Quinoline ............... | — | 130·0 | 112·0 | 113·0 |
| Pyridine ..... ......... .. | 100·0 | 100·0 | 100·0 | 100·0 |
| Quinoline .................. | 12·3 | 10·5 | 16·6 | 14·7 |
| 2-Methylquinoline ...... | 2·7 | — | 4·0 | 8·0 |

Taking into consideration the great difference of the conditions and the effect of the solvent on the reaction (Menschutkin, *loc. cit.*, and Pinner and Franz, *Ber.*, 1905, **38**, 1539), the general agreement between the ratios is remarkable. It suggests that within certain limits the nature of the influence of the constitution on the rate of reaction is independent of the conditions.

2. Several good examples of "space-filling" by groups in proximity to the *N*-atom appear to be indicated, for example:

| | | | |
|---|---|---|---|
| (*a*) Dimethylaniline (1)......... | 1·08 | Diethylaniline (3) ............ | 0·094 |
| Methylethylaniline (2) ... | 0·71 | Methylpropylaniline (4) ...... | 0·48 |
| Benzylmethylaniline (6)... | 0·123 | | |

Here the influence of the position of the methyl group in (3) and (4) is analogous to the difference in the reactivity between methyl propyl ketone and diethyl ketone with various reagents, the numerical ratios being of much the same order of magnitude; whilst the differences between (1) and (2) agree in some measure with the differences between the reactivities of the analogous ketones. The benzyl group has, as might be expected, a larger hindering effect than the propyl group.

(*b*) The influence of a substituent in the ortho-position in relation to the *N*-atom is shown with:

| | | | |
|---|---|---|---|
| Dimethylaniline (1) ......... | 1·08 | *iso*Quinoline (17)............... | 0·486 |
| Dimethyl-*o*-toluidine (9) ... | 0·057 | Quinoline (16) .................. | 0·063 |

It may also be noted that whilst the ratio:

$$\frac{\text{methyltetrahydroquinoline}}{\text{quinoline}} = 6{\cdot}5,$$

the ratio:

$$\frac{\text{methyltetrahydroquinaldine}}{\text{quinaldine}} = 2{\cdot}3,$$

which may be explained if it is assumed that the steric hindrance of the methyl group attached to the nitrogen atom is increased by the presence of a substituent in the 2-position (compare dimethylaniline and diethylaniline).

3. It is evident, however, that although these effects are so marked, stereochemical influences are not the only factors of importance in the mechanism of this reaction. The constants:

| | | | |
|---|---|---|---|
| Dimethylaniline | 1·08 | Dimethyl-*p*-toluidine | 2·8 |
| Methylacetanilide | 0·032 | *p*-Bromodimethylaniline | 0·284 |
| Dimethyl-*m*-toluidine | 1·54 | Dimethyl-*p*-aminobenzaldehyde | 0·04 |

indicate what may perhaps be called the "polar" effect of the groups attached to the nitrogen atom. The amount of this effect seems to be comparable in a general way with the effect of the same grouping on the affinity constants of the tertiary bases, although the data in regard to the latter are somewhat scanty (compare Veley, T., 1908, **93**, 2122; Walker and Ashton, T., 1895, **67**, 576).

The ratios:

| | | | |
|---|---|---|---|
| Quinoline | 0·063 | Quinaldine | 0·035 |
| Methyltetrahydroquinoline | 0·410 | Methyltetrahydroquinaldine | 0·083 |

seem to point to a similar conclusion.

It would appear, then, that an assumption of the existence of two influences—(*a*) stereochemical and (*b*) "polar"—is sufficient to explain all the present results.

The former appears to be much the larger factor of the two, and when both come into play is always dominant, for example:

| | | | |
|---|---|---|---|
| (*a*) Dimethylaniline | 1·08 | Quinoline | 0·063 |
| (*b*) Diethylaniline | 0·09 | *iso*Quinoline | 0·486 |
| (*c*) Dimethyl-*o*-toluidine | 0·057 | | |

(*b*) and (*c*) are much stronger bases than (*a*), and quinoline is a stronger base than *iso*quinoline. Thus, although the influence of the polar factor would tend to make the numbers for (*b*) and (*c*) larger than that for (*a*), the stereochemical factor appears to be so great as to much more than neutralise this effect.

It must be noted, however, that Moore's results (*loc. cit.*) on the reactivity of primary, secondary, and tertiary aliphatic amines are not all capable of such simple explanation—the cases of ammonia and trimethylamine being anomalous.

The general effect of the stereochemical factor is, of course, easily explained according to modern views of steric hindrance. The effect of the "polar" factor on the course of the reaction is not clear, and it is hoped that further exact measurements of its effect may lead to a better understanding of the state of the bases in solution.

4. (*a*) It was thought possible that the presence of an ethylene linking in a group attached to the nitrogen atom might have an effect on the reactivity of the base. The results so far obtained indicate that such effect, if any, is very slight. Compare:

| | |
|---|---|
| Methylpropylaniline | 0·48 |
| Methylallylaniline | 0·35 |

In this connexion it is interesting to note that Wedekind and Paschke (*Ber.*, 1910, **43**, 1310) find that replacing the propyl group in phenylbenzylmethylpropylammonium iodide by an allyl group does not affect the rate of decomposition.

(*b*) The constant for benzylideneaniline is not a satisfactory one; secondary decompositions undoubtedly occur, the odour of benzaldehyde being distinctly perceptible. At the same time, the numbers obtained, in view of their general similarity to those for dimethylaniline, etc., are in general accord with the formation of a quaternary ammonium compound containing a double bond attached to the nitrogen atom.

5. The exact significance of the constants for methylacetanilide and acetylpiperidine is perhaps not quite clear; but it is difficult to resist the conclusion that the bimolecular reaction which is being measured is the formation of the quaternary ammonium salt.

Wedekind states ("Stereochemie," 1907, p. 14) that methylacetanilide and methyl iodide do not combine with one another, although he observed (*Annalen*, 1901, **318**, 98) that some reaction does take place at about 250°, yielding a substance difficult to purify.

The only other evidence available on the formation of this type of compound was published recently by Dehn (*J. Amer. Chem. Soc.*, 1912, **34**, 1399) while the present investigation was in progress. This author has studied the action of acetyl chloride on tertiary bases in anhydrous ether solution; but although it would appear that pyridine acetyl chloride was obtained in a state of purity, it might be suggested that none of the other compounds was sufficiently pure to justify any definite conclusion as to its composition.

6. Owing to the fact that so many of the tertiary bases are liquids, and that the allied compounds which they are likely to contain as impurities are very similar in physical constants, it is often difficult to obtain a simple criterion of purity. It is suggested that a measurement of the reaction-velocity with allyl bromide, in view of the accuracy possible, the convenience of the conditions, and the small amount of material required, will supply the best criterion for purity of tertiary bases.

In conclusion, the author desires to acknowledge the assistance which he received from the late Dr. H. O. Jones, F.R.S., who suggested the investigation of this problem, and also to thank Prof. W. J. Pope, F.R.S., for his advice and encouragement.

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## LXVIII.—*Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. Part I. Resolution of Phenylmethylethylazonium Iodide into Optically Active Components.*

By BAWA KARTAR SINGH.

LEBEL first suggested that quaternary ammonium salts containing no asymmetric atom other than one of quinquevalent nitrogen could exist in optically active modifications (*Compt. rend.*, 1891, **112**, 724), but the experimental evidence upon which the view was based is now known to be erroneous (Pope and Read, T., 1912, **101**, 519). The first definite case of the existence of stereoisomerism of the kind indicated was described by Pope and Peachey (T., 1899, **75**, 1127), and consisted in the resolution of phenylbenzylmethylallylammonium iodide into optically active isomerides. A number of quaternary ammonium compounds have since been resolved by the method of Pope and Peachey.

In the present paper the resolution of a member of another type of enantiomorphous compound, namely, an asymmetric azonium iodide, is described; the work was undertaken at the suggestion of the late Dr. H. O. Jones.

The quaternary azonium compounds have the general formula $R_1R_2R_3XN\cdot NH_2$, in which X represents a halogen atom, and in them also the optical activity is associated with the presence of an asymmetric nitrogen atom. Besides the fact that such compounds are capable of resolution, as was to be expected from theoretical considerations, some other interesting points have arisen from the present investigation; these are chiefly concerned with the difference in the latent additive activity of the two nitrogen atoms when they are directly linked, as in the case of the compounds under examination, and when they are separated by a sufficiently long chain of other groups. To explain such differences a simple hypothesis is developed.

The azonium compounds examined were produced by the action of alkyl iodides on unsymmetrical disubstituted hydrazines in two different ways, and the same compounds resulted in each case. This, therefore, disposes of the view put forward by LeBel (*Compt. rend.*, 1899, **129**, 548) that the order in which an alkyl group is introduced is material, and establishes that no isomerides other than the two optical antipodes are formed in this way. This is an important fact, as it has bearing on the question of configuration of quinquevalent nitrogen, about which, however, much uncertainty still prevails.

The observations on the action of alkyl iodides on unsymmetrical disubstituted hydrazines, which are recorded below, have made clear that the union of the alkyl iodide takes place at the *α*, and not the *β*, nitrogen atom, since when the order of introduction of the alkyl group is varied, the same end-product results. This is quite in harmony with the observations of Harries and Haga (*Ber.*, 1898, **31**, 56) on the direct action of alkyl iodides on hydrazine hydrate, in which it has been shown that the alkyl groups attach themselves only to one of the two nitrogen atoms, producing compounds of the type $\begin{array}{c}\mathrm{N{\cdot}RH}\\ |\\ \mathrm{NH_2}\end{array}$, $\begin{array}{c}\mathrm{N{\cdot}R_2}\\ |\\ \mathrm{NH_2}\end{array}$, and finally $\begin{array}{c}\mathrm{N{\cdot}R_3I}\\ |\\ \mathrm{NH_2}\end{array}$.

These observations may be explained by the hypothesis that it is not possible for both the nitrogen atoms to become quinquevalent at the same time owing to steric interference or hindrance. Hydrazine dihydrochloride, $\begin{array}{c}\mathrm{NH_3Cl}\\ |\\ \mathrm{NH_3Cl}\end{array}$, is, however, known, but here the possibility of steric hindrance does not occur. Some experimental evidence is available which may be adduced in favour of this hypothesis. It might be expected that the free amino-group in the azonium compounds, $\mathrm{R_3N}{<}\begin{smallmatrix}\mathrm{X}\\ \mathrm{NH_2}\end{smallmatrix}$, would react with acids ($HX_1$) to yield salts, but all attempts to isolate salts of the type

$$\mathrm{R_3N}{<}\begin{smallmatrix}\mathrm{X}\\ \mathrm{NH_2,HX}\end{smallmatrix},$$

were unsuccessful. Furthermore, the platini- and the auri-chlorides of the general formulæ $(R_3N{\cdot}NH_2,HCl)_2PtCl_6$ and

$$(R_3N{\cdot}NH_2,HCl)AuCl_4$$

respectively are not produced, the compounds which are obtained containing the free amino-group, namely, $(R_3N{\cdot}NH_2)_2PtCl_6$ and $(R_3N{\cdot}NH_2)AuCl_4$.

This behaviour is again in harmony with the platinichloride of hydrazine itself, namely, $(NH_3{\cdot}NH_2)_2PtCl_6$, and of other disubstituted hydrazines. It has also been shown that the non-basic character of the amino-group is the result of the quinquevalency of the adjacent nitrogen atom, for it has been found that phenylethylhydrazine hydrochloride, $C_6H_5{\cdot}N(C_2H_5){\cdot}NH_2,HCl$, does not combine with methyl iodide, whereas the free base reacts with methyl iodide to give the azonium compound, $C_6H_5{\cdot}N(C_2H_5)(CH_3)(NH_2)I$.

Harries has further shown (*Ber.*, 1894, **27**, 702) that by the action of methyl iodide on phenyldimethylhydrazine, phenyltrimethylazonium iodide, $C_6H_5{\cdot}N(CH_3)_2I{\cdot}NH{\cdot}CH_3$, is produced, and it has also been found (compare Meyer and Jacobson, "Organ. Chemie," Band II., p. 311) that by the action of methyl iodide on phenyltrimethylhydrazine, $C_6H_5{\cdot}N(CH_3){\cdot}N(CH_3)_2$, in which both the nitrogen atoms are tertiary, the diquaternary azonium compound is not produced. The case is, however, different when the two nitrogen atoms are not directly linked, but are separated by a sufficiently long chain of methylene groups; both of them can then become quinquevalent at the same time, as in the cases of the ethylenedikairolinium di-iodides (*Ber.*, 1903, **36**, 1163) and trimethylenebisphenylmethylethylammonium iodide (*Ber.*, 1910, **43**, 2707). The fact that the trimethylene diquaternary ammonium compounds, in which the nitrogen atoms are further apart, are much more readily formed than the ethylene diquaternary ammonium compounds, is additional evidence in support of the hypothesis suggested. Although the facts cited seem to be sufficient to warrant the above view, it is intended to subject it to a further experimental study.

The resolution of phenylmethylethylazonium iodide was effected by the aid of several optically active acids. The *d*-camphor-β-sulphonate of the base was prepared by boiling a mixture, in equivalent proportions, of the azonium iodide and the silver salt with ethyl acetate (Pope and Peachey's method). The hydrogen *d*-tartrate and the hydrogen *d*-camphorate were prepared by half neutralising the azonium hydroxide with the corresponding acids. From what has been already said, it is clear that the acid radicle in these salts takes the place of the iodine of the iodide or the hydroxyl group of the hydroxide. In all the three cases examined, the less soluble salt which separates out on fractional crystallisation contains the lævo-base. The *d*-camphor-β-sulphonate gives the maximum molecular rotatory power for the *l*-phenylmethylethylazonium ion, $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N-$, as $[M]_D$ about $-16°$, the hydrogen *d*-tartrate as about $-30°$, and the hydrogen *d*-camphorate as about $-6°$.

The low values obtained for the molecular rotatory powers for the optically active ion, $(C_6H_5)(C_2H_5)(CH_3)(NH_2){\cdot}N-$, are rather noteworthy. For the sake of comparison, the value of $[M]_D$ for $(C_6H_5)(C_2H_5)(CH_3)NCl{\cdot}OH$, 41° (J. Meisenheimer, *Ber.*, 1908, **41**, 3966), and that for $(C_6H_5)(C_2H_5)(CH_3)(C_7H_7)NI$, 64·4° (Wedekind and Fröhlich, *Ber.*, 1906, **39**, 4437), may be cited, but this comparison is of little value as the molecular rotatory power is so greatly influenced by the chemical constitution of the compound.

Autoracemisation occurs in the case of these compounds; it takes place rapidly in the case of phenylmethylethylazonium *d*-camphorsulphonate, the aqueous solution becoming partly racemic within twenty-four hours. In the case of the hydrogen *d*-tartrate the inversion occurs very slowly; the active lævo-iodide which is obtained from the hydrogen *d*-tartrate also undergoes a partial racemisation on keeping in alcoholic solution. The hydrogen *d*-camphorate, which is very slowly resolved, racemises within twenty hours of making up the aqueous solution.

## EXPERIMENTAL.

Phenylethylhydrazine, $C_6H_5{\cdot}N(C_2H_5){\cdot}NH_2$, is obtained by dissolving sodium in the calculated quantity of phenylhydrazine contained in a distillation flask, distilling off the aniline and any excess of phenylhydrazine at 180° under diminished pressure, and treating the resulting sodium phenylhydrazine with ethyl iodide (Michaelis, *Ber.*, 1898, **30**, 2810). The phenylethylhydrazine is purified by conversion into its hydrochloride; this melts at 146—147°, and not at 137°, as stated by Michaelis. (Found, Cl = 20·78. Calc., Cl = 20·58 per cent.)

### *Phenylmethylethylazonium Iodide,* $(C_6H_5)(C_2H_5)(CH_3)(NH_2)NI$.

This substance was prepared by two methods: (*a*) *By the action of methyl iodide on phenylethylhydrazine.*—Phenylethylhydrazine hydrochloride (43·1 grams) was treated with potassium hydroxide, the liberated base extracted with ether, the solution dried over potassium hydroxide, and most of the ether evaporated off; one molecular proportion of methyl iodide (35·5 grams) was then added, and the mixture cooled in ice. On the addition of a little ether, white crystals began to appear, and the whole set to a solid cake in the course of two days. The crude product (53 grams) melted at 114—115°, and was recrystallised from hot alcohol; the purified azonium iodide melted and decomposed at 119°. The cooling mentioned is necessary, and if omitted, the yield becomes poor, and a dark-coloured product results. The azonium iodide is soluble in water, less so in alcohol, somewhat soluble in hot chloroform, and insoluble in benzene or ether. On keeping for some time it turns blue, but the melting point remains unchanged.

(*b*) *By the action of ethyl iodide on phenylmethylhydrazine.*—

Phenylmethylhydrazine (10·3 grams) was mixed with one molecular proportion of ethyl iodide (13·2 grams); the mixture was cooled in ice, and on the addition of a little ether a white turbidity was produced, which on rubbing became crystalline. After three days the crystalline product was collected, washed with ether, and dried in a vacuum desiccator. The crude product (11·8 grams) melted and decomposed at 106—108°, and was recrystallised from hot alcohol; the purified azonium iodide melted at 119° with decomposition. A mixture of the azonium iodides obtained by the two different methods gave the same melting point; the first method of preparation gave much the better yield:

0·14385 gave 0·2047 $CO_2$ and 0·0725 $H_2O$. C=38·81; H=5·6.
0·1517 „ 13·65 c.c. $N_2$ (moist) at 28·2° and 758 mm. N=9·9.
0·2747 „ 0·2313 AgI. I=45·48.
0·2858 „ 0·2420 AgI. I=45·76.
$C_9H_{15}N_2I$ requires C=38·84; H=5·45; N=10·1; I=45·61 per cent.

### *Action of Methyl Iodide on Phenylethylhydrazine Hydrochloride.*

Phenylethylhydrazine hydrochloride (2 grams), dissolved in chloroform, was mixed with methyl iodide (2 grams). The mixture was at first cooled in ice, and was afterwards allowed to remain at the ordinary temperature for three days without any crystals appearing; on evaporation on the water-bath, practically all the phenylethylhydrazine hydrochloride used, melting at 147°, was recovered; thus, no combination occurs between methyl iodide and phenylethylhydrazine hydrochloride, whilst the azonium compound is formed if the free base is mixed with methyl iodide under similar conditions.

### *Phenylmethylethylazonium Hydroxide,*
### $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N\cdot OH$.

This substance is prepared by the action of moist silver oxide on an aqueous solution of phenylmethylethylazonium iodide. The mixture is agitated vigorously for some time at the ordinary temperature, and after filtration, a strongly alkaline aqueous solution of the hydroxide is obtained. The hydroxide is obtained as a colourless syrup, which does not crystallise on allowing the solution to evaporate spontaneously in a vacuum desiccator; on keeping for some time it becomes coloured, with slow production of minute gas bubbles.

On heating the syrupy hydroxide in an oil-bath up to 130°, it decomposes with evolution of ethylene; water is also produced, and the decomposition may be represented thus:

$$(C_6H_5)(C_2H_5)(CH_3)(NH_2)N\cdot OH = C_6H_5\cdot N(CH_3)\cdot NH_2 + C_2H_4 + H_2O.$$

It is to be noted that the methyl group does not split off, as is generally the case, but remains attached to the nitrogen atom. The residual oil is strongly alkaline, and attempts made to identify phenylmethylhydrazine as its acetyl derivative were unsuccessful; it is inferred that the secondary hydrazine produced undergoes further decomposition.

The subject was not pursued further owing to lack of material.

### *Phenylmethylethylazonium* d-*Camphor-β-sulphonate*, $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N{\cdot}SO_3{\cdot}C_{10}H_{15}O$.

The finely powdered azonium iodide (15 grams) was added in small quantities at a time to one molecular proportion of finely powdered silver *d*-camphor-*β*-sulphonate dissolved in boiling ethyl acetate moistened with a few drops of water on the water-bath. The contents of the flask were kept shaken, and after the addition of the whole of the iodide heating was continued for another half-hour to complete the reaction. The ethyl acetate was then distilled off, and the solid residue consisting of the azonium camphorsulphonate and silver iodide transferred to a Soxhlet apparatus and extracted with ethyl acetate until only silver iodide remained behind. The crude camphorsulphonate (17 grams) obtained in this way melted at 133—134°, and after being again extracted with acetone and crystallised, it melted at 134—135°:

0·1200 gave 0·2640 $CO_2$ and 0·0853 $H_2O$. C = 59·99; H = 7·9.

$C_{19}H_{30}O_4N_2S$ requires C = 59·69; H = 7·85 per cent.

The camphorsulphonate was crystallised several times from acetone, and its rotatory power determined, with the following result:

0·3334 gram, made up to 21·1 c.c. with water, gave, in a 2-dcm. tube at 28°, $\alpha_D$ +0·295°, whence $[\alpha]_D$ +9·34° and $[M]_D$ + 35·7°.

The observations were made thirty minutes after solution.

The molecular rotatory power of the *d*-camphorsulphonic ion is $[M]_D$ +51°, whence the basic ion has approximately $[M]_D$ −15·3°. On preservation, the rotatory power of the solution gradually increased until after twenty-four hours the constant value $[M]_D$ +52° was attained.

Determinations of rotatory power made with another sample independently prepared and fractionally recrystallised from a mixture of acetone and ethyl acetate gave the following result:

0·4385 gram, made up to 20·2 c.c. with water, gave $\alpha_D$ +0·425° in a 2-dcm. tube at 29°, whence $[\alpha]_D$ +9·79° and $[M]_D$ +37·4°.

The observation was made fifteen minutes after solution, and after twenty-five minutes the value $[M]_D$ +41·45° was obtained. The rotatory power became constant at the value for the acid ion within twenty-four hours.

### *Phenylmethylethylazonium Platinichloride,*
### $[(C_6H_5)(C_2H_5)(CH_3)(NH_2)N]_2PtCl_6$.

On adding platinic chloride solution to a concentrated aqueous solution of the above camphorsulphonate, acidified with concentrated hydrochloric acid, an orange-coloured, crystalline substance separates. On crystallisation from hot water containing hydrochloric acid it is obtained in arborescent, orange-coloured needles, melting and decomposing at 159°. On keeping for some time the salt becomes dark brown, and the melting point falls:

0·1221 gave 0·0333 Pt. Pt=27·27.
$C_{18}H_{30}N_4Cl_6Pt$ requires Pt=27·46 per cent.

### *Phenylmethylethylazonium Aurichloride,*
### $[(C_6H_5)(C_2H_5)(CH_3)(NH_2)N]AuCl_4$.

On the addition of gold chloride in hydrochloric acid solution to a strong aqueous solution of the above camphorsulphonate, a yellow, crystalline substance is precipitated; this is practically insoluble in cold water, but moderately so in hot water, from which solvent, in the presence of hydrochloric acid, it crystallises in golden-yellow, stout prisms, melting and decomposing at 97°. This salt also changes colour on keeping, turning into a deep violet, hygroscopic substance:

0·1606 gave 0·06465 Au. Au=40·26.
$C_9H_{15}N_2Cl_4Au$ requires Au=40·23 per cent.

### *Phenylmethylethylazonium Hydrogen* d-*Tartrate,*
### $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N{\cdot}C_4H_5O_6$.

One molecular proportion of phenylmethylethylazonium iodide is dissolved in alcohol, the solution agitated with a slight excess of the calculated quantity of moist silver oxide for some time at the ordinary temperature, and then filtered into an alcoholic solution containing one molecular proportion of tartaric acid. The alcoholic filtrate is concentrated on the water-bath, and then treated with ether until a white turbidity is produced; this on being rubbed becomes crystalline. The solid substance is purified by recrystallisation from alcohol, and forms colourless, thin prisms, which melt at about 80° to a viscid liquid:

0·14275 gave 0·2555 $CO_2$ and 0·0934 $H_2O$. C = 48·82; H = 7·27.
0·1178 ,, 9·25 c.c. $N_2$ (moist) at 24° and 761·2 mm. N = 8·81.
$C_{30}H_{20}O_6N_2$ requires C = 52·00; H = 6·66; N = 9·33 per cent.
$C_{30}H_{20}O_6N_2,1H_2O$ requires C = 49·05; H = 6·92; N = 8·80 per cent

The salt thus appears to contain one molecule of water of crystallisation.

The hydrogen *d*-tartrate was recrystallised from a mixture of alcohol and ether, and a determination of its rotatory power gave the following results:

0·5072 gram, made up to 22 c.c. with water, gave, in a 2-dcm. tube at 25°, $\alpha_D + 0·59°$, whence $[\alpha]_D + 12·8°$ and $[M]_D + 40·7°$.

After several more crystallisations the following value was obtained:

0·4498 gram, made up to 20·95 c.c. with water, gave, in a 2-dcm. tube at 30°, $\alpha_D + 0·16°$, whence $[\alpha]_D + 7·21°$ and $[M]_D + 22·9°$.

The mean value for the hydrogen tartrate ion, $C_4H_4O_6H-$, is $[M]_D + 42°$, and consequently the value for the basic ion,

$$(C_6H_5)(C_2H_5)(CH_3)(NH_2)N,$$

is $[M]_D - 30°$ approximately.

The results of rotatory-power determinations made with a sample prepared independently and fractionally recrystallised from a mixture of alcohol and ether gave the following results. The substance was dissolved in water, and made up to 19·9 c.c. at 23°. The rotatory-power determinations were carried out in a 2-dcm. tube, and the observations were made about thirty minutes after making up the solution:

| | $\alpha_D$. | $[\alpha]_D$. | $[M]_D$. |
|---|---|---|---|
| 1st recrystallisation: | | | |
| 0·2845 gram substance ...... | +0·377° | +13·25° | +42·1° |
| 2nd recrystallisation: | | | |
| 0·5113 gram substance ...... | +0·519° | +10·15° | +32·3° |
| 3rd recrystallisation: | | | |
| 0·4194 gram substance ...... | +0·396° | +9·42° | +30·0° |
| after 3¾ hours ............ | 0·42 | 9·98 | 31·7 |
| ,, 21 ,, ............ | 0·423 | 10·0 | 31·8 |
| ,, 28 ,, ............ | 0·40 | 9·49 | 30·2 |
| Final recrystallisation: | | | |
| 0·3662 gram substance ...... | +0·259° | +7·04° | +22·4° |
| after 25 hours ............... | 0·276 | 7·5 | 23·9 |

The values of $[M]_D$ given above are calculated for the composition $C_{13}H_{20}O_6N_2,H_2O$.

### l-*Phenylmethylethylazonium Iodide.*

This salt was precipitated in very minute crystals when the solution of the above tartrate (having $[M]_D + 22{\cdot}4°$) was rendered faintly alkaline with sodium carbonate solution, and then treated with solid potassium iodide. It was recrystallised from a mixture of alcohol and ether, and melted and decomposed at 115—116°:

0·1161 gram, made up in alcohol to 12 c.c., gave, in a 1-dcm. tube at 24°, $\alpha_D - 0{\cdot}05°$, whence $[\alpha]_D - 5{\cdot}2°$ and $[M]_D - 14{\cdot}4°$.

The observations were made about thirty minutes after solution. After forty-two hours the values obtained were $\alpha - 0{\cdot}03°$, $[\alpha]_D - 3{\cdot}1°$, and $[M]_D - 8{\cdot}6°$. Some racemisation thus occurs with the active iodide in alcoholic solution.

### *Phenylmethylethylazonium Hydrogen* d-*Camphorate,*
### $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N{\cdot}C_{10}H_{15}O_4$.

One molecular proportion of the azonium iodide was dissolved in alcohol, and treated with a slight excess of moist silver oxide at the ordinary temperature. After being thoroughly agitated for some time it was filtered into an alcoholic solution containing one molecular proportion of *d*-camphoric acid. The resulting solution was evaporated on the water-bath as far as possible, a turbid liquid containing a little metallic silver being thus obtained, which was again filtered. On the addition of ether an oil separates, which, after remaining for a few hours, deposited a considerable quantity of colourless, prismatic crystals. The oily matter was again dissolved in alcohol with the addition of sufficient ether to produce the white turbidity, and on allowing to remain for some time it became crystalline. On recrystallisation from hot alcohol the salt was obtained in rhombic plates, melting and decomposing at 178—179°. For analysis, the salt was dried in the steam-oven:

0·1335 gave 0·3162 $CO_2$ and 0·1010 $H_2O$. C = 64·6; H = 8·41.

$C_{19}H_{30}O_4N_2$ requires C = 65·14; H = 8·57 per cent.

The rotatory power of the salt decreases very slowly with successive crystallisations, and becomes constant after about seven recrystallisations. In the following determinations the substance was dissolved in water, made up to 19·9 c.c., and examined in a 2-dcm. tube at 23° about thirty minutes after making up the solution:

| | $\alpha$. | $[\alpha]_D$. | $[M]_D$. |
|---|---|---|---|
| 1st recrystallisation: | | | |
| 0·1608 gram substance ...... | +0·275° | +17·0° | +59·5° |
| 2nd recrystallisation: | | | |
| 0·2046 gram substance ...... | +0·327° | +15·9° | +55·7° |
| 4th recrystallisation: | $\alpha_D$. | | |
| 0·2865 gram substance ...... | +0·468° | +16·25° | +56·9° |
| 5th recrystallisation: | | | |
| 0·2218 gram substance ..... | +0·362° | +16·24° | +56·8° |
| 7th recrystallisation: | | | |
| 0·1256 gram substance ...... | +0·199° | +15·77° | +55·2° |
| after 20 hours ............... | 0·219 | 17·35 | 60·7 |

The mean value for the acid camphoric ion, $C_{10}H_{14}O_4H-$, is $[M]_D$ +61·4° (Everatt, T., 1908, **93**, 1233), and consequently the mean value for the basic ion is about $[M]_D$ −6·2°.

Most of the rotatory-power determinations were carried out with the Landolt-Lippich triple-field polarimeter purchased out of a special grant made by the late Eastern Bengal and Assam Government, of which grateful acknowledgment is made here. I have also much pleasure in thanking my friend and colleague, Mr. E. R. Watson, for the kindly treatment and encouragement in my work which I have received from him.

The further study of this and other azonium iodides is in progress.

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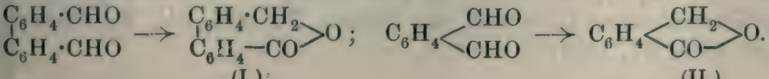
# LXIX.—*The Formation of Cyclic Compounds from Derivatives of* 2 : 2′-*Ditolyl.*

### By JAMES KENNER.

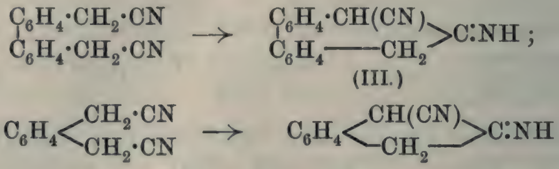
FROM an earlier paper (Kenner and Turner, T., 1911, **99**, 2101) it appeared that a close relationship existed between the derivatives of 2 : 2′-ditolyl and those of *o*-xylene. Thus, 2 : 2′-dialdehydodiphenyl underwent condensation in presence of alkali hydroxide with the production of an ε-lactone (I), a reaction which was exactly analogous to the production of phthalide (II) from *o*-phthalaldehyde in similar circumstances:



$$\begin{matrix}C_6H_4\cdot CHO\\ C_6H_4\cdot CHO\end{matrix} \longrightarrow \begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4-CO\end{matrix}\!>O;\quad C_6H_4<\begin{matrix}CHO\\ CHO\end{matrix} \longrightarrow C_6H_4<\begin{matrix}CH_2\\ CO-\end{matrix}>O.$$

(I.) (II.)

Further, the formation of 1-imino-2-cyano-3 : 5-dibenzo-$\Delta^{3:5}$-*cyclo*-heptadiene (III) from ωω′-dicyano-2 : 2′-ditolyl under the influence of sodium ethoxide corresponded with the reaction observed by Moore and Thorpe (T., 1908, **93**, 165) in the case of *o*-xylylene dicyanide:



$$\begin{array}{l}C_6H_4\cdot CH_2\cdot CN\\ C_6H_4\cdot CH_2\cdot CN\end{array} \longrightarrow \begin{array}{l}C_6H_4\cdot CH(CN)\\ C_6H_4\text{——}CH_2\end{array}\!\!>C{:}NH\,;$$

(III.)

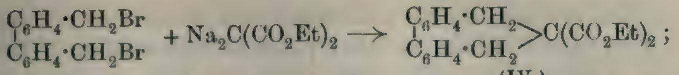
$$C_6H_4{<}\begin{array}{l}CH_2\cdot CN\\ CH_2\cdot CN\end{array} \longrightarrow C_6H_4{<}\begin{array}{l}CH(CN)\\ CH_2\text{—}\end{array}\!\!>C{:}NH$$

These observations, coupled with the formation of an anhydride and an imide from diphenic acid, led to the suggestion that the 2 : 2′-position in diphenyl derivatives is an effective ortho-position, and that the seven-membered doubly unsaturated rings produced in the above reactions are more closely allied to saturated *cyclo*-pentane derivatives than to those of *cyclo*heptane.

These views have received important support from the fact (since communicated to the author by Dr. J. F. Thorpe) that it is not possible to synthesise derivatives of *cyclo*hexane from αε-dicyanopentane under the conditions of the imino-condensation just mentioned. The reaction therefore constitutes a sensitive test of the proximity of the ω-cyanogen and the 1-methylene radicles in such compounds—as, indeed, would be expected in view of the entire absence of "constraint" from the conditions under which the reaction is carried out.

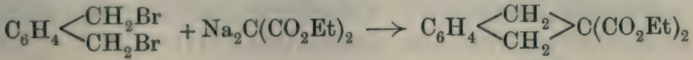
The experiments now to be described were undertaken in order to accumulate further evidence in connexion with the synthesis of cyclic compounds from derivatives of 2 : 2′-ditolyl, and as a result it may be said that the relationship indicated above is completely established, so far as the formation of seven-membered rings is concerned. Further, an illustration is supplied of the fact that, contrary to the opinion so widely entertained, the mere number of carbon atoms may not be the most important factor in determining whether ring formation can or can not take place.

In the first place, it was shown that ωω′-dibromo-2 : 2′ditolyl condenses with ethyl malonate in presence of sodium ethoxide with the production of *diethyl* 3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-1 : 1-*dicarboxylate* (IV) in a manner which recalls the formation of diethyl hydrindenedicarboxylate (V) from *o*-xylylene dibromide (Perkin, T., 1888, **53**, 7), and of diethyl pentamethylenedicarboxylate from αδ-dibromobutane (Haworth and Perkin, T., 1894, **65**, 96; Stauss, *Ber.*, 1894, **27**, 1229):



$$\begin{array}{l}C_6H_4{\cdot}CH_2Br\\ |\\ C_6H_4{\cdot}CH_2Br\end{array} + Na_2C(CO_2Et)_2 \longrightarrow \begin{array}{l}C_6H_4{\cdot}CH_2\\ |\\ C_6H_4{\cdot}CH_2\end{array}\!\!>C(CO_2Et)_2\,;$$

(IV.)

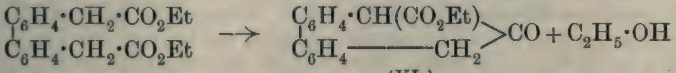


$$C_6H_4\!<\!\begin{array}{l}CH_2Br\\ CH_2Br\end{array} + Na_2C(CO_2Et)_2 \longrightarrow C_6H_4\!<\!\begin{array}{l}CH_2\\ CH_2\end{array}\!\!>C(CO_2Et)_2$$

(V.)

In the case of hexamethylene dibromide, Haworth and Perkin (*loc. cit.*, p. 599) found that only a very small proportion was converted into the *cyclo*heptane derivative, the main product being the open-chain tetraethyl octanetetracarboxylate. In the present instance, however, the tendency to form the seven-membered ring is so great that even in the presence of two molecular proportions of ethyl malonate the reaction takes the same course as indicated above and one-half of the ethyl malonate is recovered unchanged.

Further, when diethyl 2 : 2′-ditolyl-ωω′-dicarboxylate is heated with sodium in benzene solution, it readily undergoes the Dieckmann condensation, and *ethyl* 3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-1-*one*-2-*carboxylate* (VI) is produced to the extent of 80 per cent. of the calculated amount:



$$\begin{array}{l}C_6H_4{\cdot}CH_2{\cdot}CO_2Et\\ |\\ C_6H_4{\cdot}CH_2{\cdot}CO_2Et\end{array} \longrightarrow \begin{array}{l}C_6H_4{\cdot}CH(CO_2Et)\\ |\\ C_6H_4\text{———}CH_2\end{array}\!\!>CO + C_2H_5{\cdot}OH$$

(VI.)

This compound gives an indigo-blue coloration with ferric chloride solution, and has pronounced acid properties, since its copper salt can be isolated by treatment with copper acetate without any precautions being taken to neutralise the acetic acid set free. This behaviour is in agreement with that of ethyl *cyclo*pentanonecarboxylate, as contrasted with the corresponding *cyclo*hexanone and *cyclo*heptanone derivatives (Dieckmann, *Annalen*, 1901, **317**, 32), but the two cases are, of course, not strictly comparable, since the presence of an adjacent benzene nucleus would in any circumstances be expected to increase the acidity of the compound now described.

In the case of this reaction it is not possible to institute a comparison with the behaviour of the corresponding *o*-xylene derivative,* because neither this, nor, indeed, any other compound not of purely aliphatic nature had hitherto been studied in this respect; but the yield obtained in the present case compares favourably with that obtained by Dieckmann (*loc. cit.*, p. 52) under similar conditions in the case of ethyl adipate (80 per cent.), whilst the yield of ethyl *cyclo*heptanonecarboxylate obtained from ethyl suberate amounted to only about 10 per cent. (Dieckmann, *loc. cit.*, p. 50).

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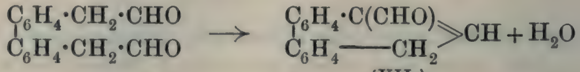
* It is intended to study the behaviour of diethyl *o*-phenylenediacetate in this respect.

A further instance of the readiness with which ring-formation of the type under discussion takes place is contained in a recent paper by Weitzenböck * (*Monatsh.*, 1913, **34**, 199), in which it is shown that ωω′-dialdehydo-2 : 2′-ditolyl is condensed by sulphuric acid to an aldehydodibenzo*cyclo*heptatriene (VII):



$$\begin{matrix} C_6H_4\cdot CH_2\cdot CHO \\ | \\ C_6H_4\cdot CH_2\cdot CHO \end{matrix} \longrightarrow \begin{matrix} C_6H_4\cdot C(CHO) \\ | \\ C_6H_4 — CH_2 \end{matrix} \gt CH + H_2O$$

(VII.)

The compounds now described, together with the dibenzo*cyclo*heptadienone previously obtained (Kenner and Turner, *loc. cit.*), render the more important derivatives of dibenzo*cyclo*heptadiene accessible by the usual methods, but the appearance of Weitzenböck's communication has necessitated the publication of the present paper before the experiments in this direction were as complete as it had been intended to make them. However, 1-*amino*-3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene* (IX) has been prepared by reduction of *cyclo*heptadienoneoxime with sodium, whilst 3 : 5-*dibenzo*-$\Delta^{1:3:5}$-cyclo-

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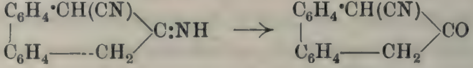
* Weitzenböck refers (*loc. cit.*, p. 218) to a compound, m. p. 222°, obtained by heating iminocyanodibenzo*cyclo*heptadiene with concentrated hydrochloric acid under pressure, and to which he is unable to assign a constitution. In conjunction with Miss E. G. Turner, I carried out a similar experiment under atmospheric pressure two years ago. It was, however, found that the product was a mixture of two compounds, one of which, m. p. 220° (over 90 per cent. of the whole) was insoluble in sodium carbonate solution, whilst the other, m. p. 219°, was soluble. The composition of each corresponded with that of the expected 2-*cyano*-3 : 5 *dibenzo*-$\Delta^{3:5}$-cyclo*heptadien*-1-*one* (VIII).



$$\begin{matrix} C_6H_4\cdot CH(CN) \\ | \\ C_6H_4 — CH_2 \end{matrix} \gt C{:}NH \longrightarrow \begin{matrix} C_6H_4\cdot CH(CN) \\ | \\ C_6H_4 — CH_2 \end{matrix} \gt CO$$

(VII.)

*Non-acid portion:*

0·1122 gave 0·3400 $CO_2$ and 0·0944 $H_2O$. C = 82·64 ; H = 4·89.

*Acid portion:*

0·1002 gave 0·3024 $CO_2$ and 0·0444 $H_2O$. C = 82·3 ; H = 4·92.

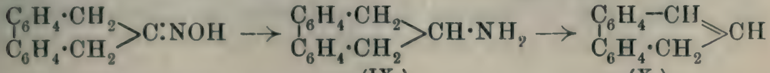
0·2063 ,, 11·6 c.c. $N_2$ at 30° and 726 mm. N = 6·27.

$C_{16}H_{11}ON$ requires C = 82·4 ; H = 4·72 ; N = 6·02 per cent.

No depression of melting point was observed when the two compounds were mixed, and the two appeared to be interconvertible ; further, the non-acid portion gave a brilliant wine-red coloration when heated with ferric chloride solution. The preliminary investigation thus seemed to show that the two compounds were desmotropically related, and the description of the experiments was deferred until the opportunity arose for a more thorough inquiry.

It may be pointed out that the numbering used by Weitzenböck in the designation of the above imino-compound is in contravention of the usual rules of the Geneva system, and as the compound in question has already been incorporated in this system (Kenner and Turner, *loc. cit.*) an alternative numbering can only lead to confusion and is therefore undesirable.

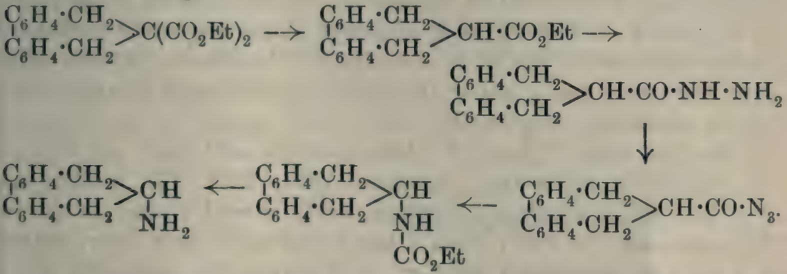
*heptatriene* (X) can be obtained by the dry distillation of the hydrochloride of the base:



$$\left.\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CH_2\end{matrix}\right>C{:}NOH \longrightarrow \left.\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CH_2\end{matrix}\right>CH\cdot NH_2 \longrightarrow \left.\begin{matrix}C_6H_4-CH\\ C_6H_4\cdot CH_2\end{matrix}\right>CH$$

(IX.) (X.)

This hydrocarbon is the analogue of indene, and, in view of the results obtained in the examination of the latter compound (Marckwald, *Ber.*, 1895, **28**, 1501; Thiele, *Ber.*, 1900, **33**, 3395; *Annalen*, 1906, **347**, 249), the further examination of dibenzo*cyclo*heptatriene is a matter of considerable interest. Unfortunately, the yields obtained by the above process are prohibitive, and attempts were therefore made to obtain dibenzo*cyclo*heptadienylamine in a more convenient manner. This object was attained by means of the series of reactions represented in outline by the following scheme:



$$\left.\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CH_2\end{matrix}\right>C(CO_2Et)_2 \longrightarrow \left.\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CH_2\end{matrix}\right>CH\cdot CO_2Et \longrightarrow \left.\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CH_2\end{matrix}\right>CH\cdot CO\cdot NH\cdot NH_2$$

$$\downarrow$$

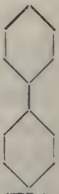
$$\left.\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CH_2\end{matrix}\right>\begin{matrix}CH\\ |\\ NH_2\end{matrix} \longleftarrow \left.\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CH_2\end{matrix}\right>\begin{matrix}CH\\ |\\ NH\\ |\\ CO_2Et\end{matrix} \longleftarrow \left.\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CH_2\end{matrix}\right>CH\cdot CO\cdot N_3.$$

All these reactions give good yields, and it is hoped that, possibly by the use of the phosphate method of Harries (*Ber.*, 1901, **34**, 300) or the exhaustive methylation method of Willstätter (*Ber.*, 1907, **40**, 3979, and other papers), dibenzo*cyclo*heptatriene may be obtained in sufficient quantity to permit of its closer study. The distillation of *barium* 3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-1-*monocarboxylate* furnished a hydrocarbon, but this was apparently not dibenzo*cyclo*heptatriene, although Perkin and Révay (T., 1894, **65**, 246) found that barium hydrindenecarboxylate is converted into indene under these conditions.

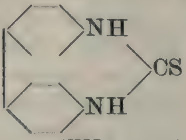
When the attempt is made to ascertain the cause of the readiness with which the formation of seven-membered rings from derivatives of 2 : 2′-ditolyl takes place, two modes of explanation suggest themselves.

The first assumes that the two benzene nuclei are not, as is usually considered and is required by the ordinary tetrahedral distribution of the valencies of the carbon atom, represented by (XI), but are inclined to one another in such a manner as to bring the carbon atoms in the 2 : 2′-position as close to each other as in the ordinary ortho-position. This assumption makes

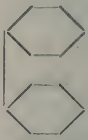
2 : 2′-ditolyl directly comparable with *o*-xylene, as indeed has now been shown is the case, and has been advocated by Kaufler (*Annalen*, 1907, **351**, 152) to explain the production of some remarkable compounds of the type shown (XII):



(XI.)



(XII.)



(XIII.)

Kaufler assumes that the configuration of diphenyl is represented as shown (XIII), but does not specify whether he considers the two benzene nuclei to be in parallel planes or coplanar. In the former case ring-formation should be equally possible with 2 : 2′-, 3 : 3′-, and 4 : 4′-derivatives of diphenyl, whilst the latter postulates the equivalence of the 2 : 2′- and the 3 : 3′-positions. Quite apart from the severe strain either alternative would impose on the carbon atoms connecting the nuclei, both would appear to be disproved by the fact that diphenyl-3 : 3′-dicarboxylic acid does not furnish an anhydride (Ullmann, *Annalen*, 1904, **332**, 73), whilst the 2 : 2′-derivative (ordinary diphenic acid) is well known to do so. This argument, however, fails if the dicarboxylic acid be in reality a 3 : 5′- as contrasted with a 3 : 3′-derivative (compare Cain, Coulthard, and Micklethwait, T., 1912, **101**, 2298), and it would be interesting to know whether 3 : 3′-dinitrodiphenyl could be converted, for instance, into an azoxy-compound or a thiocarbamide derivative corresponding with XII. The author has not yet had the opportunity of studying other 3 : 3′- or 4 : 4′-derivatives in this respect.

The second explanation was brought forward in the previous communication, and, accepting the ordinary formula, was based on the view that the presence of double bonds in six- and seven-membered rings diminishes the strain and makes them more comparable with the saturated five-membered ring.*

According to this explanation, the mean strain in the doubly unsaturated heptamethylene ring is 5°2′, and it would therefore be expected that a five-membered ring would be formed in preference to a seven-membered ring of this type. Experiments carried out in this laboratory by Miss A. M. Mathews, B.Sc., are in agreement with this inference; 2 : 3 : 2′ : 3′-diphenyltetracarboxylic acid is converted by acetyl chloride into the dianhydride (XIV), and no sign of the compound (XV) could be detected:

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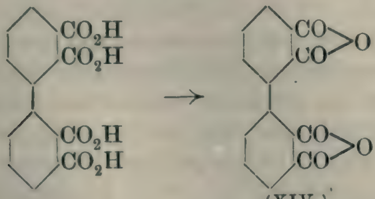
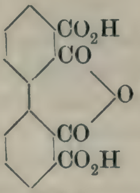
* In this way, the mean strain in the benzene molecule was calculated as 2°38′; this calculation has since been carried out, apparently independently, by Böeseken (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **14**, 1066; compare *Ann. Reports*, 1912, p. 114), in connexion with some interesting speculations in regard to the benzene problem.

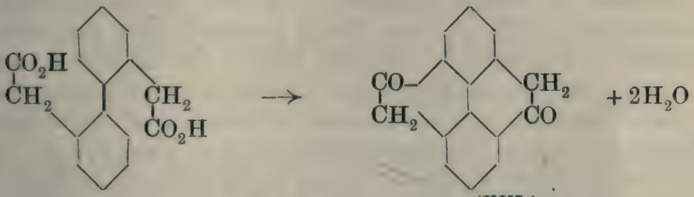


(XIV.)



(XV.)

Since this hypothesis lays stress on the presence of the double bonds, it follows that the simultaneous formation of seven-membered rings in the 2 : 2′- and the 6 : 6′-positions of diphenyl should not be possible under the conditions used in the above experiments, and it will be necessary to carry out experiments in this direction. The synthesis of dihydroxypyrene * (XVI), recently recorded by Weitzenböck (*loc. cit.*):



(XVI.)

cannot be considered as evidence against this contention, since it is well known that six-membered rings are formed in the majority of cases almost as readily as five-membered rings. The reaction is of interest, however, as showing that the 2 : 2′- and the 6 : 6′-positions in diphenyl are relatively equivalent. This fact, on the hypothesis of inclined nuclei discussed above, can only be explained if the two benzene nuclei be in parallel planes. As this assumption is untenable (with the reservation already indicated), the theory that the nuclei are inclined must, in the author's opinion, be regarded with a very considerable measure of reserve, although it must be conceded that the production of Kaufler's thiocarbamide derivatives does not admit of any other obvious explanation.

Experiments have also been made with the view of synthesising derivatives of dibenzo*cyclo*octadiene. Thus, as *o*-xylylene dibromide and disodium ethanetetracarboxylate condense with the formation of a tetrahydronaphthalene derivative (Perkin, T., 1888, **53**, 7), it was hoped that ωω′-dibromo-2 : 2′ditolyl might behave in a similar manner:

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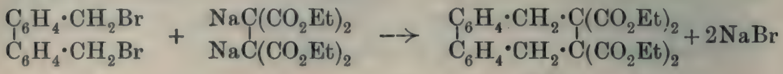
* Experiments having for their object the synthesis of compounds of similar type have been in progress for some time in this laboratory.



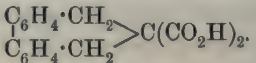
$$\begin{array}{l}C_6H_4\cdot CH_2Br\\ |\\ C_6H_4\cdot CH_2Br\end{array} + \begin{array}{l}NaC(CO_2Et)_2\\ |\\ NaC(CO_2Et)_2\end{array} \longrightarrow \begin{array}{l}C_6H_4\cdot CH_2\cdot C(CO_2Et)_2\\ | \qquad\qquad\quad |\\ C_6H_4\cdot CH_2\cdot C(CO_2Et)_2\end{array} + 2NaBr$$

(XVII.)

A product was actually isolated, the percentage composition of which agreed with this constitution (XVII), but the determination of its molecular weight by the cryoscopic method has thrown doubt on the accuracy of this formula, and the reaction must therefore be further investigated. It may be remarked that the mean strain in a *cyclo*octadiene ring amounts to 8°49′, which is considerably less than that in the saturated *cyclo*heptane ring.

## EXPERIMENTAL.

### 3 : 5-*Dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-1 : 1-*dicarboxylic Acid*,



$$\begin{array}{l}C_6H_4\cdot CH_2\\ |\\ C_6H_4\cdot CH_2\end{array}\!\!>C(CO_2H)_2.$$

A solution of diethyl malonate (8 grams) in freshly distilled anhydrous ether (120 c.c.) was added gradually to a hot solution of sodium (2·3 grams) in absolute alcohol (30 c.c.) in a reflux apparatus. Before the separation of diethyl sodiomalonate from the warm mixture had commenced, a solution of ωω′-dibromo-2 : 2′-ditolyl (17 grams) in absolute ether (140 c.c.) was run in. The mixture at once became turbid, owing to the production of sodium bromide, and, after the initial vigorous reaction had subsided, the mixture was heated on the water-bath for three hours. After filtration, the ether was removed from the solution, which was neutral to litmus, by distillation. The residual oil consisted of almost pure diethyl dibenzo*cyclo*heptadienedicarboxylate, and slowly became converted into a mass of crystals. In order to isolate the dicarboxylic acid, the oil, dissolved in absolute alcohol (250 c.c.), was returned to the flask containing the sodium bromide, and the mixture was then heated on the water-bath with a solution of potassium hydroxide (10 grams) in water (10 c.c.) until hydrolysis was complete, the operation requiring about half an hour. Unduly prolonged treatment resulted in partial elimination of carbon dioxide, for the final product had a low melting point, but gave satisfactorily pure material when subsequently converted into the monocarboxylic acid. The product of hydrolysis was worked up in the usual manner, the dicarboxylic acid being precipitated from the solution of its potassium salt after the latter had been extracted with ether to remove impurities, which rendered the solution slightly turbid. The yield of crude product was nearly 90 per cent. of that calculated. After crystallisation from dilute alcohol, the acid was obtained in colourless prisms, which melted at 205° with loss of carbon dioxide:

0·1106 gave 0·2922 $CO_2$ and 0·0514 $H_2O$. C = 72·05; H = 5·16.

$C_{17}H_{14}O_4$ requires C = 72·34; H = 4·97 per cent.

The *diethyl* ester, isolated in the manner already described, was purified by crystallisation from light petroleum (b. p. 40—60°), and formed rhombic crystals, which melted at 64°:

0·1464 gave 0·3992 $CO_2$ and 0·0872 $H_2O$. C = 74·37; H = 6·62.

$C_{21}H_{22}O_4$ requires C = 74·54; H = 6·51 per cent.

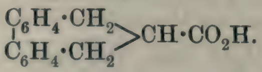
It was recovered unchanged after several days from its solution in alcohol, saturated with ammonia.

The *dihydrazide* was, however, produced when the diethyl ester was heated with hydrazine hydrate in alcoholic solution for several hours on the water-bath, and crystallised from alcohol in lustrous leaflets, which melted at 246°:

0·1556 gave 24·1 c.c. $N_2$ at 17° and 748 mm. N = 18·03.

$C_{17}H_{18}O_2N_4$ requires N = 18·01 per cent.

### 3 : 5-*Dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-1-*carboxylic Acid*,



$$\begin{matrix} C_6H_4\cdot CH_2 \\ | \\ C_6H_4\cdot CH_2 \end{matrix} > CH\cdot CO_2H.$$

This acid was produced when the dicarboxylic acid just described was heated in an oil-bath at 210° until the evolution of carbon dioxide had ceased. The product was cooled and dissolved in sodium carbonate solution. After extraction with ether, the solution was acidified, and the precipitated acid obtained in good yield. The acid was purified by crystallisation from dilute alcohol, from which it separated in flat needles, melting at 158°:

0·1486 gave 0·4376 $CO_2$ and 0·0808 $H_2O$. C = 80·31; H = 6·04.

$C_{16}H_{14}O_2$ requires C = 80·67; H = 5·88 per cent.

The *barium* salt is best prepared by the gradual addition of an alcoholic solution of the acid to a hot solution of barium hydroxide, and separates from its solution in opaque clusters of needles, containing water of crystallisation, which is given up at 180°:

0·3144 gave 0·0392 $H_2O$ and 0·1052 $BaSO_4$. $H_2O$ = 12·53; Ba = 19·40.

$(C_{16}H_{13}O_2)_2Ba,5H_2O$ requires $H_2O$ = 12·8; Ba = 19·67 per cent.

When the anhydrous barium salt was heated under diminished pressure, it decomposed without any charring, and a colourless, viscous oil was produced which did not distil. The oil was isolated in the usual manner by extraction with ether, and in the course of two months a few elongated hexagonal plates separated. These could not, however, be separated from the remainder of the material. No semicarbazone could be prepared from the product, which therefore did not contain a ketone. When, however, it was treated with alcoholic picric acid solution, a *picrate* was obtained, which crystallised in reddish-brown prisms, melting at 147—149°. The further examination of this compound was postponed until it could be compared with the picrate of dibenzo*cyclo*heptatriene, when it was found that a mixture of the two picrates melted at 110°. It therefore followed that the decomposition of the barium salt had not taken place in the same manner as that observed by Perkin and Révay in the case of hydrindenecarboxylic acid, which was converted into indene (T., 1894, **65**, 246). The nature of this reaction will be the subject of closer investigation.

The *methyl* ester was prepared by saturating a cold solution of the acid in methyl alcohol with dry hydrogen chloride, and working up the mixture in the usual manner after three days. The ester was obtained as a highly refractive colourless liquid of high viscosity, boiling at 288°/181 mm., and gradually crystallised to radiate aggregates of plates, which melted at 44—45°:

0·2006 gave 0·5934 $CO_2$ and 0·1126 $H_2O$. C = 80·68; H = 6·23.

$C_{17}H_{16}O_2$ requires C = 80·95; H = 6·35 per cent.

The *ethyl* ester resulted when the acid was esterified by means of sulphuric acid. It boiled at 244°/43 mm., and was a highly refractive viscous liquid, which did not solidify:

0·1746 gave 0·5184 $CO_2$ and 0·1058 $H_2O$. C = 80·98; H = 6·73.

$C_{18}H_{18}O_2$ requires C = 81·20; H = 6·76 per cent.

The *chloride* was prepared in the usual manner by treating the acid with phosphorus pentachloride and boiled at 235°/60 mm.:

0·3876 gave 0·2144 AgCl. Cl = 13·68.

$C_{16}H_{13}OCl$ requires Cl = 13·84 per cent.

The *amide* was best prepared by the gradual addition of the chloride, previously heated to 100° to increase its mobility, to a cold aqueous ammonia solution (D 0·880) in a mortar. Each drop of the chloride was well triturated with the solution before any further addition was made, and the reaction was finally completed by warming the mixture on the water-bath. Owing to its high viscosity, the chloride is practically unattacked by ammonium carbonate in the cold, and this method is therefore unsuitable for the preparation of the amide.

It also results when the methyl ester is heated under pressure with aqueous ammonia solution (D 0·880) at 130°, but the yield is only moderate.

By crystallisation from methyl alcohol, the amide was obtained in prisms, melting at 158°:

0·1626 gave 8·4 c.c. $N_2$ at 18° and 728 mm. N = 5·83.

$C_{16}H_{15}ON$ requires N = 5·91 per cent.

It did not dissolve in sodium hypochlorite solution, and the attempt to prepare the corresponding amine from it by the Hofmann method was therefore abandoned.

The *hydrazide* was prepared by heating the ethyl ester with excess of hydrazine hydrate in alcoholic solution on the water-bath until the mixture set to a solid mass when cooled. The hydrazide was separated by filtration from the liquor, and the latter usually furnished a further quantity of hydrazide after further heating. The compound was purified by crystallisation from alcohol, from which it separated in matted needles, melting at 176°. The hydrazide is only sparingly soluble in water, but readily so in cold chloroform or hot alcohol:

0·1613 gave 16·4 c.c. $N_2$ at 19·5° and 725 mm. N = 11·37.

$C_{16}H_{16}ON_2$ requires N = 11·11 per cent.

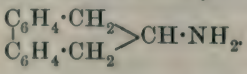
### *Tetrabromo*-3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-1-*carboxylic Acid.*

A thin layer of finely ground dibenzo*cyclo*heptadienecarboxylic acid was exposed in a desiccator to the action of bromine vapour. After one week, the pasty product was transferred to a vacuum desiccator containing solid potassium hydroxide. It was then found that the acid had increased in weight by an amount which was about 5 per cent. more than that corresponding with the absorption of four atomic proportions of bromine. The tetrabromo-acid was sparingly soluble in alcohol, acetic acid, or the usual organic solvents, but dissolved easily in epichlorohydrin, and separated from this solvent in small clusters of opaque prisms, melting at 272°:

0·2366 gave 0·3217 AgBr. Br = 57·91.

$C_{16}H_{10}O_2Br_4$ requires Br = 57·77 per cent.

### 1-*Amino*-3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*,

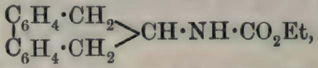


$$\left.\begin{array}{l} C_6H_4\cdot CH_2 \\ | \\ C_6H_4\cdot CH_2 \end{array}\right> CH\cdot NH_2.$$

The preparation of this compound was effected in two ways, namely, from the hydrazide of dibenzo*cyclo*heptadienecarboxylic acid and from the oxime of dibenzo*cyclo*heptadienone.

(i) A solution of the hydrazide (5·5 grams) in hot absolute alcohol (50 c.c.) was rapidly cooled, and treated at 0° with a solution of hydrogen chloride (1 gram) in absolute alcohol (10 c.c.). On shaking, the crystals of the hydrazide rapidly gave place to those of its hydrochloride, and the mixture became much more fluid. Amyl nitrite (3 grams) was then added, and after some time the mixture was allowed to regain the ordinary temperature, whereby almost everything passed into solution, with the exception of a few well-defined, transparent, colourless, rectangular prisms of the azide. After the yellow solution had been boiled until the evolution of nitrogen had ceased, the alcohol was removed by evaporation on the water-bath. The heating was continued for some time in order to remove the amyl esters as completely as possible, and the residual oil (5 grams) was then stirred with a little warm alcohol until crystallisation set in. The crystals were then pressed and further purified by solution in light petroleum (b. p. 90—120°). Yield, 4 grams.

3 : 5-*Dibenzo*-$\Delta^{3:5}$-cyclo*heptadienylurethane*,



$$\begin{array}{l} C_6H_4\cdot CH_2 \\ | \\ C_6H_4\cdot CH_2 \end{array}\!\!>CH\cdot NH\cdot CO_2Et,$$

forms clusters of small prisms, melting at 88°:

0·2301 gave 10·4 c.c. $N_2$ at 16° and 736 mm. N = 5·19.
$C_{18}H_{19}O_2N$ requires N = 4·98 per cent.

The urethane readily undergoes hydrolysis when it is heated with concentrated hydrochloric acid under pressure for six hours at 150°, dibenzo*cyclo*heptadienylamine hydrochloride being produced. If the crude oily urethane is hydrolysed without further purification, it is necessary to stir the dark-coloured oil formed in the reaction with ether, which extracts dibenzo*cyclo*heptadienecarboxylic acid. The presence of this acid is presumably due to the production of its ethyl ester in small amount (about 20 per cent.), when the azide is boiled with alcohol.

(ii) A boiling solution of dibenzo*cyclo*heptadienoneoxime (11 grams) in absolute alcohol (200 c.c.) was reduced by the gradual addition of sodium (20 grams) in the course of one hour. If necessary, the dissolution of the sodium was completed by the addition of a small quantity of absolute alcohol, and the mixture was then diluted and subjected to steam distillation. The distillate was acidified with hydrochloric acid and evaporated to dryness, whereby the hydrochloride of the base (5 grams) was left. The later portions of the distillate contained another product (possibly dibenzo*cyclo*heptadienone), which was readily separated from the hydrochloride by extracting the concentrated solution with ether.

*Dibenzo*cyclo*heptadienylamine hydrochloride* forms lustrous needles, moderately soluble in dilute hydrochloric acid. It melts at 287°, and decomposes about 300°:

0·1928 gave 10·2 c.c. $N_2$ at 21° and 731 mm. $N=5·94$.

$C_{15}H_{15}N,HCl$ requires $N=5·70$ per cent.

The *platinichloride* is a canary-yellow precipitate, which could not be obtained in a crystalline condition. It melts at 268°:

0·3576 gave 0·0838 Pt. $Pt=23·38$.

$(C_{15}H_{15}N)_2H_2PtCl_6$ requires $Pt=23·58$ per cent.

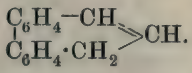
An aqueous solution of the hydrochloride gave a white precipitate with ammonium oxalate, and a yellow one with potassium dichromate solution. No precipitate was produced with ferric chloride or with potassium iodide.

*Acetyldibenzo*cyclo*heptadienylamine* was prepared by heating the hydrochloride with acetic anhydride and sodium acetate at 140°. After crystallisation from dilute alcohol, it formed slender, silky needles, melting at 147°:

0·1668 gave 8·4 c.c. $N_2$ at 17° and 739 mm. $N=5·79$.

$C_{17}H_{17}ON$ requires $N=5·56$ per cent.

### 3 : 5-*Dibenzo*-$\Delta^{1:3:5}$-cyclo*heptatriene*,



$$\begin{array}{l} C_6H_4-CH \\ \vert \\ C_6H_4\cdot CH_2 \end{array}\!\!>\!CH.$$

Dibenzo*cyclo*heptadienylamine hydrochloride was heated in a drawn-out test-tube until decomposition was complete. Only a small amount of oil distilled over, and this was converted by treatment with a saturated alcoholic picric acid solution into a reddish-brown picrate. A larger quantity was obtained from the oil contained in the test-tube, after separation from the ammonium chloride also present, by extraction with ether and drying in the usual manner. The yield was only moderate.

*Dibenzo*cyclo*heptatriene picrate* crystallises from alcoholic solution in copper coloured needles, which melt at 137°:

0·1460 gave 0·3200 $CO_2$ and 0·0530 $H_2O$. $C=59·78$; $H=4·03$.
0·1524 ,, 13·8 c.c. at 12° and 715 mm. $N=10·2$.

$C_{15}H_{12},C_6H_3O_7N_3$ requires $C=59·86$; $H=3·56$; $N=9·98$ per cent.

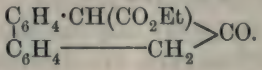
### *Diethyl* 2 : 2'-*Ditolyl*-$\omega\omega'$-*dicarboxylate*,
### $CO_2Et\cdot CH_2\cdot C_6H_4\cdot C_6H_4\cdot CH_2\cdot CO_2Et$.

This compound was prepared by esterifying the dicarboxylic acid in the presence of sulphuric acid in the usual manner. After crystallisation from light petroleum (b. p. 60—80°), it was obtained in large, rhombic crystals, which melted at 49°:

0·1774 gave 0·4778 $CO_2$ and 0·1060 $H_2O$. $C=73·45$; $H=6·64$.

$C_{20}H_{22}O_4$ requires $C=73·65$; $H=6·75$ per cent.

### *Ethyl* 3 : 5-*Dibenzo*-$\Delta^{3:5}$-cyclo*heptadien*-1-*one*-2-*carboxylate*,



$$\left.\begin{array}{l} C_6H_4\cdot CH(CO_2Et) \\ \big| \\ C_6H_4\text{———}CH_2 \end{array}\right> CO.$$

Sodium powder (2·1 grams), prepared in presence of toluene in the usual manner, was covered with dry benzene (150 c.c.) in a reflux apparatus, and diethyl 2 : 2′-ditolyl-ωω′-dicarboxylate (14·6 grams) was then added. The mixture was raised to the boiling point, and a vigorous reaction at once set in. After this had moderated, the heating was continued for about one hour, by which time all the sodium had disappeared, and the mixture began to bump violently, owing to the separation of sodium ethoxide. The reddish liquid was then decomposed by dilute sulphuric acid, the oily layer separated and washed, and the crude ester isolated by distilling off the benzene. By shaking the ethereal solution of the residual oil with aqueous copper acetate solution, the copper salt of the condensation product was precipitated, whilst any unchanged ester was retained by the ether. Yield, 11·2 grams.

The *copper* salt is a dirty light green powder, dark green in solution. It is readily soluble in chloroform, epichlorohydrin, or benzene, sparingly so in ether, and insoluble in acetone, alcohol, or water. It separates from a mixture of epichlorohydrin with alcohol in an indistinctly crystalline condition, and melts at 253°. By decomposition with nitric acid and careful ignition:

0·3701 gave 0·0463 CuO. Cu = 10·01.

$(C_{18}H_{15}O_3)_2Cu$ requires Cu = 10·23 per cent.

The free ester was obtained by shaking the solution of the copper salt in benzene with dilute sulphuric acid. Its alcoholic solution is coloured indigo-blue by ferric chloride. When the attempt was made to distil it under diminished pressure (30 mm.) it decomposed, and nothing passed over. The residue in the flask no longer gave a coloration with ferric chloride.

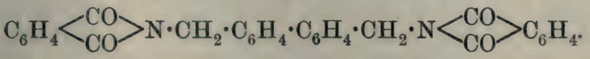
### *Condensation of ωω′-Dibromo-*2 : 2′*-ditolyl with Tetraethyl Ethanetetracarboxylate.*

Finely powdered dibromoditolyl (3·4 grams) and tetraethyl ethanetetracarboxylate (3·18 grams) were heated with a solution of sodium (0·45 gram) in absolute alcohol (40 c.c.) at 120—140° under pressure for five hours. The product, which was neutral to litmus, was freed from alcohol by evaporation. The residual oil was stirred with cold water, and quickly solidified. By crystallisation from light petroleum (b. p. 40—60°), rectangular blocks (1·2 grams) were obtained, which melted at 108·5°:

0·1256 gave 0·3120 $CO_2$ and 0·0758 $H_2O$. C = 67·74; H = 6·71.
0·1160 „ 0·2878 $CO_2$ „ 0·0662 $H_2O$. C = 67·67; H = 6·34.
$C_{28}H_{32}O_8$ requires C = 67·76; H = 6·45 per cent.

The composition of the product thus corresponds with that of the expected tetraethyl dibenzo*cyclo*octadienetetracarboxylate, but determinations of the molecular weight by the cryoscopic method in benzene solution, kindly carried out by Mr. W. A. Silvester (Found, 364, 387. Calc., 496), are not in agreement with this formula, and it will therefore be necessary to examine this compound more closely.

### *ωω′-Diphthalimino-2 : 2′-ditolyl,*



$$C_6H_4<\substack{CO\\CO}>N\cdot CH_2\cdot C_6H_4\cdot C_6H_4\cdot CH_2\cdot N<\substack{CO\\CO}>C_6H_4.$$

This compound was readily obtained when dibromoditolyl was heated with two molecular proportions of potassium phthalimide at 150° for one hour. The solid mass was powdered, extracted with hot water, and the residual diphthalimino-derivative purified by crystallisation from glacial acetic acid. It forms prisms, which melt at 256°:

0·1962 gave 11·0 c.c. $N_2$ at 30° and 716 mm. N = 6·17.
$C_{30}H_{20}O_4N_2$ requires N = 5·93 per cent.

By hydrolysis with concentrated hydrochloric acid at 180°, *ωω′-diamino-2 : 2′-ditolyl dihydrochloride* is produced.

The reactions of the compounds described above are under investigation, and the general question of ring formation from ditolyl derivatives is being studied along the lines indicated in this paper.

In conclusion, the author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which covered part of the expenses of this investigation.

THE UNIVERSITY,
SHEFFIELD.

# LXX.—*The Vapour Pressures of the Lower Alcohols and their Azeotropic Mixtures with Water. Part I. Ethyl Alcohol.*

By Richard William Merriman, M.A.

An azeotropic mixture is a mixture of liquids which distils at a constant temperature, when the pressure is kept constant, without change of composition. The study of such mixtures, since the pioneering work of Roscoe and Dittmar (T., 1859, **12**, 128), has been confined to a few workers, partly because of the tedious nature of the work, and partly because no explanation of the formation of such mixtures has been brought forward, so that the results obtained cannot be used in testing the validity of theoretical deductions.

The work has, however, led to many important technical applications, such as the preparation of strong acids (Roscoe and Dittmar, *loc. cit.*; Roscoe, T., 1860, **13**, 146; 1862, **15**, 270), the preparation of chloroform for medical use (Wade and Finnemore, T., 1904, **85**, 938), and the preparation of absolute alcohol (Young, T., 1902, **81**, 707). The recent paper by Forster and Withers (this vol., p. 266) on Vaubel's phenyldi-imine has called the attention of organic chemists to the importance of always bearing in mind the possibility of the formation of such mixtures.

The azeotropic mixtures which the lower alcohols form with water at atmospheric pressure have been studied by various workers since the time of Erlenmeyer (*Annalen*, 1863, **126**, 307), and were completely worked out by Young and Fortey (T., 1902, **81**, 717).

The present work was commenced with the idea that the study of the binary azeotropic mixtures of a homologous series of alcohols and water, at different pressures, might produce data which would be of assistance in the formulation of a theoretical explanation of the existence of such mixtures.

The compositions of the azeotropic mixtures of ethyl alcohol and water, at various pressures, have already been determined (Wade and Merriman, T., 1911, **99**, 997). The results followed the rule, from which there are only one or two exceptions, that the percentage of the constituent of lower boiling point, in a mixture of minimum boiling point, increases as the pressure decreases. The work of Forster and Withers (*loc. cit.*) also supports the rule

In the present communication, determinations of the vapour pressure of ethyl alcohol by the dynamic method are described, and the view is expressed that this method gives more trustworthy results than other methods. Determinations of the boiling points of the azeotropic mixtures, made up according to the results previously obtained (Wade and Merriman, *loc. cit.*), are also given, and are compared with the boiling points of dry alcohol, at the same pressures.

### I.—*Preparation and Density of Absolute Alcohol.*

(*a*) Ten litres of 95 per cent. alcohol were boiled in a copper drum for twenty-four hours with 4 kilos. of quick-lime made from marble. On distilling the product, spirit containing about 0·5 per cent. of water was obtained. This formed the stock, which was carefully dried, as required, in batches of 700 grams.

(*b*) 700 Grams of the 99·5 per cent. alcohol were boiled on the water-bath, under a reflux condenser, with 150 grams of quick-lime made from marble, taking the usual precautions for preventing the absorption of atmospheric moisture. After six hours, the product was distilled from the water-bath, a double spray trap being fixed on to the flask. The first 50 grams were rejected; the distillate obtained by boiling almost to dryness (about 600 grams) had a density of 0·80630 0°/4°, and thus contained 0·006 per cent. of water. By continuing the heating, more alcohol slowly distilled from the apparently dry lime. In this way 25 grams were obtained; the density was 0·80634 0°/4°, corresponding with 0·02 per cent. of water. When the main fraction was distilled, the contents of the flask were probably at a temperature of not more than 80°, but when the last few grams were slowly distilled from the solid residue, the temperature must have reached 100°. It follows that calcium hydroxide at 100°, in the presence of alcohol, is partly dehydrated. This observation was repeated several times. Therefore in the preparation of absolute alcohol, both the first and last fractions should be rejected.

(*c*) The alcohol of specific gravity 0·80630 0°/4° was again treated with lime, and the density of the main fraction was 0·80628 0°/4°. Another treatment with lime left the density unchanged.

(*d*) On treating this alcohol with metallic calcium, carefully washed with dry alcohol, the density still remained the same.

(*e*) 200 Grams of the alcohol of density 0·80628 0°/4° were mixed with 3 grams of washed calcium and distilled through an eight-section Young evaporator column. No alteration in the density took place.

(*f*) Starting once more with 99·5 per cent. alcohol and using metallic calcium instead of lime, the final product with density 0·80628 0°/4° was reached with much greater difficulty and loss of material. Many other dehydrating agents were tried, but lime was found to be by far the most efficient. In all, about forty samples of absolute alcohol were prepared, with density 0·80628 0°/4°, and no subsequent treatment would reduce the density.

The densities were determined in the manner recently described (Wade and Merriman, T., 1912, **101**, 2429).

This density confirms the value 0·80627 0°/4° obtained by Young (T., 1902, **81**, 717), and 0·80628 0°/4° by Klason and Norlin (*Arkiv. Kem. Min. Geol.*, 1906, **8**, No. 24, 1). The final product contained only small traces of acetaldehyde (less than 1 in 5000), and as this small amount cannot affect the density or boiling point, it was not thought worth while to run the risk of introducing other impurities in an endeavour to remove it.

(*g*) Samples of alcohol were prepared from potassium ethyl sulphate by Klason and Norlin's method (*loc. cit.*). They had the same densities and boiling points as the previous samples.

## II.—*The Vapour Pressure of Ethyl Alcohol.*

The best method of determining vapour pressures is to distil large quantities of the pure liquid through a Young evaporator column, using efficient means for maintaining constant pressures (Wade and Merriman, T., 1911, **99**, 984). A distillation, at the rate of one drop per second, can be carried out when the boiling point is six or seven degrees above room temperature, without superheating the thermometer at the top of an eight-section column. Therefore if a small room kept at −7° were available, the boiling points could

TABLE I.

*Experimental Boiling Points of Ethyl Alcohol.*

| Pressure in mm. | Boiling point. | Pressure in mm. | Boiling point. |
|---|---|---|---|
| 30·8 | 14·34° | 448·8 | 65·55° |
| 34·5 | 16·10 | 498·7 | 68·00 |
| 37·6 | 17·50 | 549·7 | 70·30 |
| 43·6 | 20·00 | 597·1 | 72·30 |
| 44·6 | 20·30 | 649·7 | 74·37 |
| 49·5 | 22·08 | 700·7 | 76·24 |
| 57·2 | 24·39 | 750·2 | 77·98 |
| 72·5 | 28·53 | 769·5 | 78·62 |
| 75·0 | 29·20 | 800·1 | 79·60 |
| 78·8 | 30·04 | 899·7 | 82·63 |
| 98·8 | 34·18 | 999·6 | 85·39 |
| 132·7 | 39·71 | 1021·8 | 86·01 |
| 150·8 | 42·23 | 1099·9 | 87·97 |
| 198·1 | 47·70 | 1199·6 | 90·30 |
| 218·1 | 49·68 | 1301·0 | 92·55 |
| 247·0 | 52·26 | 1401·7 | 94·62 |
| 300·3 | 56·46 | 1501·1 | 96·56 |
| 347·8 | 59·66 | 1599·9 | 98·39 |
| 400·5 | 62·89 | 1679·0 | 99·76 |

be determined from 0° upwards. The lowest temperature obtainable by the author was 7°, so that another method had to be used for temperatures below 14°. The Anschütz thermometers used in this work had been compared with standards, and the temperatures are reduced to the hydrogen scale in the latitude of Paris. At least, two different thermometers were used at each pressure.

For low pressures, the apparatus used in the case of ethyl acetate (Wade and Merriman, T., 1912, **101**, 2438) was modified by adding a second thermometer, the bulb of which was just above the surface of the liquid, and was wrapped in cotton wool which dipped in the liquid. The whole apparatus was loosely wrapped in cotton wool, and no external heat was used during the experiment. When the pressure was kept constant for some time, the two thermometers registered the same temperature, after being corrected for the change of zero due to the vacuum (Ramsay and Young, *Phil. Trans.*, 1884, **173**, ii, 472).

Every care must be taken to keep the pressure constant, as the thermometer in the liquid is slower than the other in reaching a new constant temperature. The reason for choosing this method is that the same apparatus is used in the study of the azeotropic mixtures at low temperatures. A mixture of known composition is placed in the flask, and after half of it has boiled away, the composition of the residue is determined.

TABLE II.

*Experimental Boiling Points of Ethyl Alcohol at Low Pressures.*

| Pressure in mm. | Boiling point. | Pressure in mm. | Boiling point. |
|---|---|---|---|
| 10·1 | −2·05° | 20·8 | 8·11° |
| 11·8 | −0·20 | 21·7 | 8·74 |
| 12·5 | +0·53 | 22·3 | 9·07 |
| 12·8 | 0·87 | 23·0 | 9·60 |
| 13·3 | 1·39 | 25·0 | 11·05 |
| 13·9 | 2·15 | 26·6 | 11·98 |
| 15·0 | 2·90 | 27·3 | 12·30 |
| 15·9 | 3·99 | 28·4 | 12·93 |
| 16·8 | 4·94 | 29·7 | 13·68 |
| 17·3 | 5·34 | 30·5 | 14·01 |
| 18·4 | 6·25 | 31·1 | 14·35 |
| 19·4 | 7·11 | | |

The first differences of the experimental results were plotted against the mean temperatures. This curve, which required only slight modification, was smoothed by means of the second difference curve. The experimental results were smoothed by its aid, and the results given in tables III, IV, and V were calculated.

## TABLE III.

*Vapour Pressures of Ethyl Alcohol from 0° to 25°.*

| Temp. | Pressure in mm. | *dp/dt.* | Temp. | Pressure in mm. | *dp/dt.* |
|---|---|---|---|---|---|
| 0° | 12·0 | 0·90 | 13° | 28·4 | 1·81 |
| 1 | 12·9 | 0·94 | 14 | 30·3 | 1·92 |
| 2 | 13·9 | 0·99 | 15 | 32·2 | 2·03 |
| 3 | 14·9 | 1·04 | 16 | 34·3 | 2·15 |
| 4 | 15·9 | 1·10 | 17 | 36·4 | 2·28 |
| 5 | 17·0 | 1·16 | 18 | 38·7 | 2·41 |
| 6 | 18·2 | 1·22 | 19 | 41·2 | 2·55 |
| 7 | 19·4 | 1·29 | 20 | 43·8 | 2·70 |
| 8 | 20·7 | 1·37 | 21 | 46·5 | 2·84 |
| 9 | 22·1 | 1·45 | 22 | 49·4 | 2·99 |
| 10 | 23·5 | 1·53 | 23 | 52·4 | 3·15 |
| 11 | 25·1 | 1·62 | 24 | 55·6 | 3·31 |
| 12 | 26·7 | 1·71 | 25 | 59·0 | 3·47 |

## TABLE IV.

*Vapour Pressures of Ethyl Alcohol from 0° to 105°.*

| Temp. | Pressure in mm. | *dp/dt.* | Temp. | Pressure in mm. | *dp/dt.* |
|---|---|---|---|---|---|
| 0° | 12·0 | 0·90 | 55° | 281·2 | 12·85 |
| 5 | 17·0 | 1·16 | 60 | 352·7 | 15·60 |
| 10 | 23·5 | 1·53 | 65 | 438·9 | 18·85 |
| 15 | 32·2 | 2·03 | 70 | 542·5 | 22·60 |
| 20 | 43·8 | 2·70 | 75 | 666·0 | 26·95 |
| 25 | 59·0 | 3·47 | 80 | 812·7 | 31·90 |
| 30 | 78·6 | 4·42 | 85 | 985·2 | 37·45 |
| 35 | 103·6 | 5·58 | 90 | 1187·0 | 43·70 |
| 40 | 134·9 | 6·95 | 95 | 1422·0 | 50·70 |
| 45 | 174·0 | 8·57 | 100 | 1694·0 | 58·40 |
| 50 | 222·2 | 10·50 | 105 | 2007·0 | 66·95 |

## TABLE V.

*Boiling Points of Ethyl Alcohol.*

| Pressure in mm. | Boiling point. | *dt/dp.* | Pressure in mm. | Boiling point. | *dt/dp.* |
|---|---|---|---|---|---|
| 50 | 22·20° | 0·3312 | **760** | **78·30** | 0·0332 |
| 100 | 34·35 | 0·1846 | 800 | 79·61 | 0·0318 |
| 150 | 42·06 | 0·1316 | 900 | 82·65 | 0·0288 |
| 200 | 47·83 | 0·1033 | 1000 | 85·42 | 0·0264 |
| 250 | 52·47 | 0·0863 | 1100 | 87·96 | 0·0244 |
| 300 | 56·41 | 0·0738 | 1200 | 90·32 | 0·0226 |
| 350 | 59·84 | 0·0645 | 1300 | 92·52 | 0·0208 |
| 400 | 62·87 | 0·0576 | 1400 | 94·58 | 0·0200 |
| 450 | 65·59 | 0·0520 | 1500 | 96·53 | 0·0189 |
| 500 | 68·06 | 0·0471 | 1600 | 98·37 | 0·0179 |
| 550 | 70·33 | 0·0437 | 1700 | 100·12 | 0·0171 |
| 600 | 72·43 | 0·0406 | 1800 | 101·78 | 0·0163 |
| 650 | 74·39 | 0·0380 | 1900 | 103·37 | 0·0156 |
| 700 | 76·24 | 0·0356 | 2000 | 104·89 | 0·0150 |

The boiling point at 760 mm. is identical with Young's value (*loc. cit.*), and those at 400 mm., 1000 mm., and 1600 mm. with the values given by Schmidt (*Zeitsch. physikal. Chem.*, 1891, **8**, 620).

As the author wished to find the most trustworthy method for the determination of a large number of vapour pressures, he thought it worth while to examine some of the results obtained by means of Ramsay and Young's method (T., 1885, **47**, 42).

Table VI gives a comparison of the present values with those of Ramsay and Young (*Phil. Trans.*, 1886, **177**, i, 155) and of Richardson (T., 1886, **49**, 762), which were all done in this way.

TABLE VI.

| Temp. | (*b.*) | (*c.*) | (*d.*) | (*e.*) | (*f.*) | (*g.*) | (*h.*) |
|---|---|---|---|---|---|---|---|
| 0° | 12·0 | 12·24 | 12·24 | — | — | 12·24 | 12·24 |
| 5 | 17·0 | 17·15 | — | 18·17 | 19·57 | 17·15 | 17·25 |
| 10 | 23·5 | 23·50 | 23·77 | 24·81 | 26·22 | 23·5 | 23·75 |
| 15 | 32·2 | 32·10 | — | 33·84 | 33·40 | 32·1 | 32·40 |
| 20 | 43·8 | 43·95 | 44·00 | 45·6 | 45·76 | 43·8 | 43·95 |
| 25 | 59·0 | 59·50 | — | 61·03 | 61·27 | 59·5 | 59·15 |
| 30 | 78·6 | 78·05 | 78·06 | 78·72 | 82·21 | 80·2 | 78·80 |

Column (*b*) gives the present results; column (*c*) those of Ramsay and Young (*loc. cit.*), which have since been modified by Young (*Sci. Proc. Roy. Dubl. Soc.*, 1910, **12**, 441), these modified values being given in column (*d*); columns (*e*) and (*f*) represent Richardson's values, calculated from his nearest experimental results.

The values of Ramsay and Young given in column (*c*) were found not to lie on a smooth curve, the value for 30° falling completely off the first difference curve. If most of the lower values are retained, that at 30° must be increased to 80·2 mm. in order to produce a smooth curve. These smoothed values are given in column (*g*). If, however, the modified values of Young are used, except that at 30°, the values given in column (*h*) are obtained on smoothing. These values agree in a remarkable way with the present values given in column (*b*), considering that each determination involves two readings of the manometer, besides those of the barometer and thermometer.

It seems, therefore, that Ramsay and Young's experimental results in the neighbourhood of 25° and 30° are somewhat inaccurate.

It will also be seen that Richardson's results given in columns (*e*) and (*f*) do not agree among themselves. The method seems to present great experimental difficulties. With the view of thoroughly testing whether Ramsay and Young's method was worth adopting as a standard, the author examined other results obtained with it. The values for acetic acid in Richardson's paper (*loc. cit.*), which purported to be fresh determinations made with a sample of the identical acid used by Ramsay and Young (T., 1885, **47**, 43), were found to be merely reprinted from the latter paper. Although a test of the method by the results of different workers was not available, Richardson himself did two series of experiments with the same sample of each liquid, in order to "check the results" (T., 1886, **49**, 762).

Typical results are given in table VII.

TABLE VII.

*Richardson's Experimental Results with the Ramsay and Young Method.*

| Substance. | Temperature. | Pressures in mm.<br>1st Experiment. | <br>2nd Experiment. |
|---|---|---|---|
| *iso*Butyl alcohol........ | 66·0° | 116·29 | 124·617 |
| | 78·7 | 226·82 | 229·45 |
| | 104·8 | 669·113 | 680·830 |
| *iso*Amyl alcohol......... | 95·65 | 193·08 | 190·41 |
| *iso*Butyric acid ......... | 143·80 | 601·49 | 552·24 |
| *iso*Valeric acid ...... ... | 133·0 | 175·159 | 174·01 |
| | 158·27 | 434·039 | 440·91 |

It will be seen that the work is not sufficiently accurate. The method was therefore not adopted, as it evidently requires prolonged practice, and as the static method is liable to give erratic results, the distillation method appears to offer the greatest chances of success, if a cold room is available for the lower temperatures.

The vapour pressures depend on the readings of three instruments. At low pressures the readings of the manometer and barometer are the most important, as a difference of 0·1 mm. means a difference of 0·1°. In this region pressures may be recorded to 0·05 mm., or in special cases to 0·01 mm. At atmospheric pressure a difference of 0·01° corresponds with a difference in pressure of 0·3 mm., and at two atmospheres with a difference of 0·6 mm. It is therefore clear that values recorded to 0·01 mm. or 0·001 mm. are meaningless. The experimental values, which should be numerous, should be smoothed by the method of first and second differences, and not by means of an empirical formula. No empirical formula * hitherto tried gives results exact enough for smoothing purposes.

## III.—*Boiling Points of the Azeotropic Mixtures of Ethyl Alcohol and Water.*

The mixtures were made up according to the values previously obtained (Wade and Merriman, T., 1911, **99**, 1002). The results are given in table VIII.

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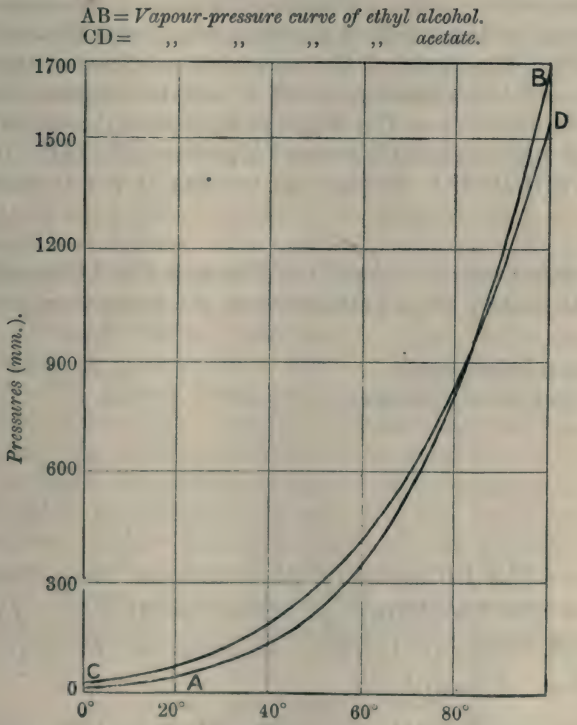
* Biot's formula, or the Ramsay and Young expression : $R = R' + a(t' - t)$, gives only approximate results. The latter is obviously inapplicable to substances such as ethyl acetate and ethyl alcohol, the vapour pressure curves of which cut each other. Water is usually chosen as the standard substance, yet its vapour pressure curve is abnormal. Even for normal substances, the calculated values frequently differ from the observed values by many times the possible experimental error.

TABLE VIII.

| Pressure in mm. | Per cent. of water in the azeotropic mixture. | Boiling point of azeotropic mixture. | Boiling point of ethyl alcohol. | Δ. | Boiling point of water. | Δ′. |
|---|---|---|---|---|---|---|
| 1451·3 | 4·75 | 95·35° | 95·58° | 0·23° | 119·14° | 23·56 |
| 1075·4 | 4·65 | 87·12 | 87·34 | 0·22 | 110·00 | 22·66 |
| 760·0 | 4·4 | 78·15 | 78·30 | 0·15 | 100·00 | 21·70 |
| 404·6 | 3·75 | 63·04 | 63·13 | 0·09 | 83·27 | 20·14 |
| 198·4 | 2·7 | 47·63 | 47·66 | 0·03 | 66·31 | 18·65 |
| 129·7 | 1·3 | 39·20 | 39·24 | 0·04 | 57·06 | 17·82 |
| 94·9 | 0·5 | 33·35 | 33·38 | 0·03 | 50·62 | 17·24 |
| 70·0 | 0·0 | — | 27·96 | 0·00 | 44·63 | 16·67 |

The column under Δ represents the differences between the boiling points of alcohol and of the azeotropic mixture; that under Δ′ gives the differences between the boiling points of alcohol and water.



The curve, drawn by plotting Δ against the pressure, is as smooth as can be expected for such small differences of temperature.

The boiling points of the pure alcohol and of the azeotropic mixture, at atmospheric pressure, are identical with the values obtained by Young and Fortey (T., 1903, **81**, 768).

An interesting point should be noticed. At 1450 mm., when the difference between the boiling points of water and alcohol is 23·56°, a distillate containing 4·75 per cent. of water is obtained on distilling a mixture of alcohol and water, but at 70 mm., when the difference between the boiling points is only 16·67°, anhydrous alcohol distils over.

Any theory of azeotropic mixtures must explain this fact, that, as the boiling points of the pure liquids approach each other, separation by fractional distillation becomes easier.

A very curious point arises in the case of ethyl acetate and ethyl alcohol. The vapour-pressure curves of these liquids cross each other at a pressure of 948·1 mm. At this pressure each liquid boils at 84·01°; at higher pressures the boiling point of ethyl acetate is above that of ethyl alcohol; at lower pressures ethyl alcohol has the higher boiling point. These liquids form an azeotropic mixture of minimum boiling point at atmospheric pressure (Wade, T., 1905, **87**, 1656). The study of the azeotropic mixtures of these liquids at high and low pressures, which is now in progress, might lead to important results. The diagram represents the vapour-pressure curves of ethyl acetate (Wade and Merriman, T., 1912, **101**, 2438) and of ethyl alcohol, showing the crossing at the above-mentioned point.

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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# LXXI.—*The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part III. Solubility of Carbon Dioxide at Pressures lower than Atmospheric.*

By Alexander Findlay and Thomas Williams, B.Sc. (1851 Exhibition Science Bursar, University College of Wales, Aberystwyth).

It has already been shown by Findlay and Creighton (T., 1910, **97**, 536) that the solubility of carbon dioxide in water is affected very markedly by the presence of colloidal substances, the solubility in presence of the latter being in some cases greater, in some cases less, than in pure water. The form of solubility curve which was obtained in those cases was such that it became of interest to ascertain the values of the solubility at pressures lower than atmospheric; and we have therefore determined the solubility at 25° of carbon dioxide in water in presence of ferric hydroxide, dextrin, starch, gelatin, egg-albumen, silicic acid, suspensions of charcoal and of silica at pressures between 25° and 760 mm. of mercury, the results obtained being communicated in the present paper.

The apparatus employed was essentially the same as that used by Findlay and Creighton, but the manometer tube was now lowered so as to allow of pressures lower than atmospheric being measured. On account of the much smaller amount of gas absorbed at the low pressures, it was necessary to diminish the dead space as far as possible, so that the necessary correction might not constitute too large a fraction of the total gas volume measured. Even by reducing the dead space to 10 c.c., which was the lowest practicable value, the correction amounts, in some cases, to about 2 per cent. of the volume measured. We cannot therefore claim the same accuracy for our present determinations of the solubility as for those previously made, but the error may be taken as not exceeding 0·5 per cent.

In carrying out a determination of the solubility at low pressures, one proceeded as follows. The absorption pipette was filled with water or colloidal solution at 25°, whilst the tube communicating with the burette was filled with carbon dioxide under atmospheric pressure. A small filtering flask was attached to the lower tube of the absorption pipette, and a few c.c. of the liquid were forced into the flask by slightly increasing the pressure on the gas. Communication between the absorption pipette and the burette was then broken, the filtering flask was exhausted, and the requisite amount of liquid (about 35 c.c.) was withdrawn from the pipette. The pressure in the absorption pipette was now about one-fifth of an atmosphere. After the liquid in the pipette had acquired the temperature of the thermostat, the pressure in the burette was lowered to a suitable value, communication was opened between the burette and the pipette, and the solubility then determined as usual.

### (*a*) *Water.*

The following values were obtained for the solubility in water of the carbon dioxide employed.

TABLE I.—*Solubility of Carbon Dioxide in Water.*

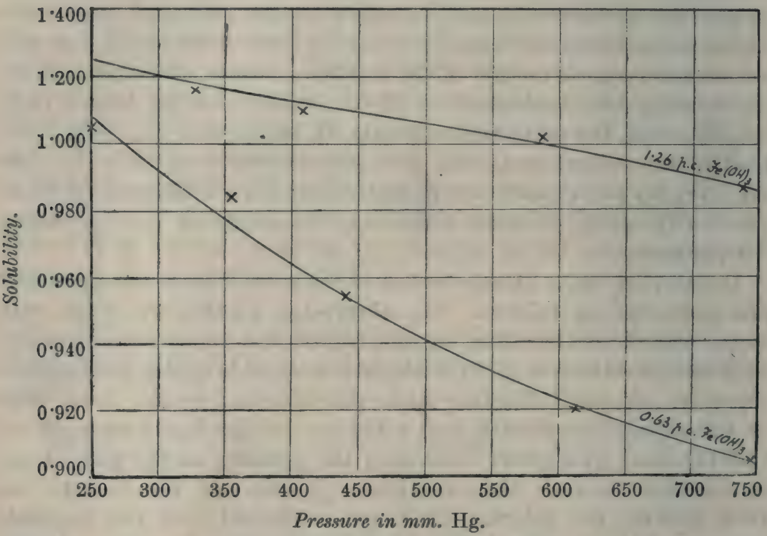
| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 271 | 392 | 495 | 667 | 768 |
| Solubility ............ | 0·816 | 0·811 | 0·816 | 0·817 | 0·817 |
| Pressure ............ | 263 | 382 | 479 | 651 | 752 |
| Solubility ............ | 0·817 | 0·814 | 0·816 | 0·816 | 0·818 |

As the mean value of the solubility therefore, we find 0·816.

### (*b*) *Ferric Hydroxide Solution.*

The ferric hydroxide solution was prepared as described by A. A. Noyes (*J. Amer. Chem. Soc.*, 1905, **37**, 94). It was freed from air by boiling under diminished pressure. The values of the solubility are given in table II (compare Fig. 1).

FIG. 1.



*Carbon dioxide and ferric hydroxide.*

TABLE II.—*Solubility of Carbon Dioxide in Ferric Hydroxide Solutions.*

Concentration: 0·63 gram of $Fe(OH)_3$ in 100 c.c. of solution. Density = 1·003.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 250 | 356 | 441 | 614 | 746 |
| Solubility ............ | 1·044 | 0·984 | 0·954 | 0·920 | 0·904 |

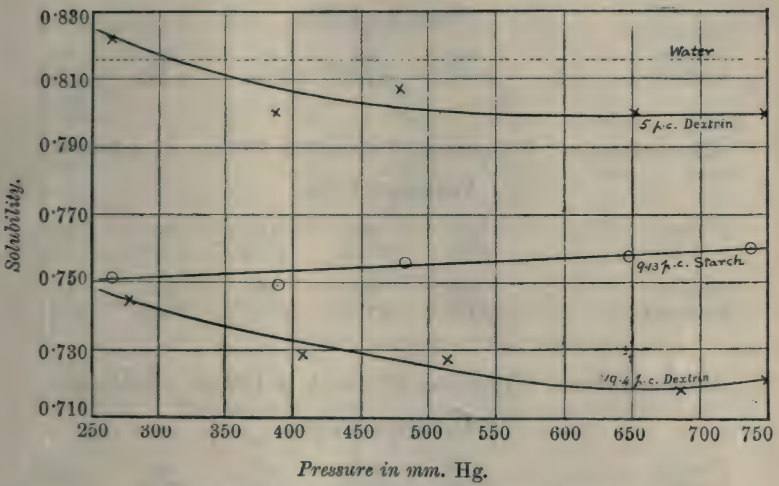
Concentration: 1·26 gram of $Fe(OH)_3$ in 100 c.c. of solution. Density = 1·006.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 233 | 328 | 409 | 587 | 740 |
| Solubility ............ | 1·286 | 1·165 | 1·107 | 1·029 | 0·989 |

### (*c*) *Dextrin.*

The dextrin employed was the purest supplied by Kahlbaum. It contained a slight amount of impurity insoluble in water. This was separated from the solutions before the latter were employed for absorbing carbon dioxide. The solutions were then rendered air-free by boiling under diminished pressure. The solubility values are given in table III (compare Fig. 2).

FIG. 2.



*Carbon dioxide in solutions of dextrin and of starch.*

TABLE III.—*Solubility of Carbon Dioxide in Dextrin Solutions.*

Concentration: 5·00 grams of dextrin in 100 c.c. of water.

Density = 1·018.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 263 | 385 | 477 | 646 | 747 |
| Solubility ............ | 0·820 | 0·802 | 0·809 | 0·800 | 0·799 |
| Pressure ............ | 267 | 389 | 480 | 656 | 759 |
| Solubility ............ | 0·823 | 0·798 | 0·804 | 0·799 | 0·799 |

Concentration: 19·4 grams of dextrin in 100 c.c. of solution.

Density = 1·065.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ...... ..... | 271 | 399 | 501 | 679 | 760 |
| Solubility ............ | 0·742 | 0·728 | 0·726 | 0·720 | 0·722 |
| Pressure ............ | 283 | 414 | 527 | 688 | 755 |
| Solubility ............ | 0·746 | 0·730 | 0·727 | 0·715 | 0·720 |

### (*d*) *Starch.*

For these experiments Kahlbaum's pure soluble starch was employed. The solutions were again rendered air-free by boiling under reduced pressure.

TABLE IV.—*Solubility of Carbon Dioxide in Solutions of Starch.* (See also Fig. 2.)

Concentration: 4·6 grams of starch in 100 c.c. of solution.

Density = 1·018.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 260 | 378 | 473 | 639 | 735 |
| Solubility ............ | 0·787 | 0·784 | 0·786 | 0·789 | 0·789 |

Concentration: 5·1 grams of starch in 100 c.c. of solution.

Density = 1·021.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 265 | 385 | 483 | 641 | 738 |
| Solubility ............ | 0·783 | 0·785 | 0·783 | 0·783 | 0·783 |
| Pressure ............ | 268 | 385 | 483 | 650 | 751 |
| Solubility ............ | 0·788 | 0·786 | 0·787 | 0·784 | 0·784 |

Concentration: 9·13 grams of starch in 100 c.c. of solution.

Density = 1·035.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 262 | 382 | 478 | 641 | 731 |
| Solubility ............ | 0·751 | 0·752 | 0·757 | 0·758 | 0·760 |
| Pressure ............ | 268 | 391 | 489 | 653 | 743 |
| Solubility ............ | 0·751 | 0·746 | 0·755 | 0·758 | 0·760 |

We were able to confirm the observation made by Findlay and Creighton that the time required to saturate starch solutions is comparatively great. Moreover, the more concentrated the starch solution, the greater was the time required to saturate it with carbon dioxide.

### (*e*) *Gelatin.*

French sheet gelatin was employed, the solutions being rendered air-free by boiling under diminished pressure. In the case of gelatin solutions, also, we were able to confirm the observation of Findlay and Creighton that saturation with carbon dioxide takes place comparatively slowly.

TABLE V.—*Solubility of Carbon Dioxide in Solutions of Gelatin.* (See also Fig. 3.)

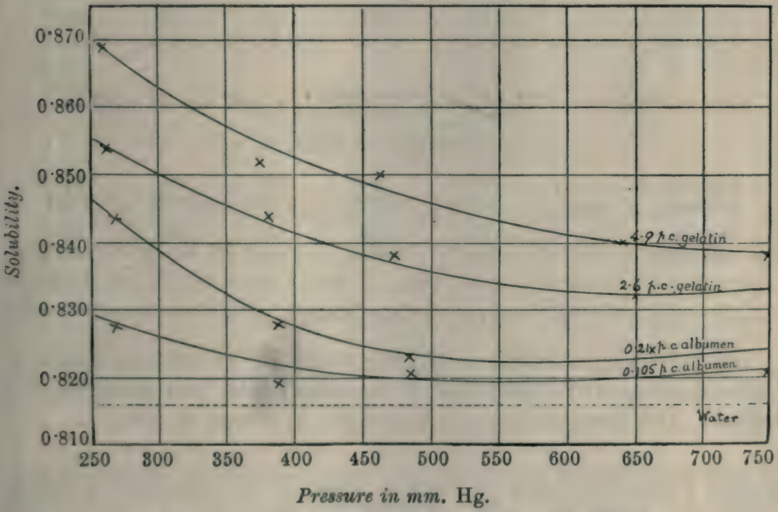
Concentration: 2·6 grams of gelatin in 100 c.c. of solution. Density = 1·006.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 264 | 383 | 471 | 651 | 762 |
| Solubility ............ | 0·855 | 0·845 | 0·837 | 0·831 | 0·833 |
| Pressure ............ | 262 | 380 | 477 | 649 | 756 |
| Solubility ............ | 0·856 | 0·847 | 0·842 | 0·832 | 0·835 |
| Pressure ............ | 264 | 380 | 470 | 651 | 759 |
| Solubility ............ | 0·850 | 0·840 | 0·836 | 0·832 | 0·833 |

Concentration: 4·9 grams of gelatin in 100 c.c. of solution. Density = 1·012.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 258 | 373 | 459 | 635 | 743 |
| Solubility ............ | 0·870 | 0·847 | 0·847 | 0·839 | 0·838 |
| Pressure ............ | 263 | 377 | 468 | 644 | 751 |
| Solubility ............ | 0·868 | 0·854 | 0·852 | 0·841 | 0·838 |
| Pressure ............ | 260 | 375 | 466 | 641 | 749 |
| Solubility ............ | 0·870 | 0·854 | 0·850 | 0·841 | 0·839 |

FIG. 3.



*Carbon dioxide in solutions of gelatin and of albumen.*

### (*f*) *Egg-Albumen.*

For these experiments Schuchardt's egg-albumen was used. This was dissolved in water filtered from an insoluble portion, and the albumen then precipitated by addition of ammonium sulphate to the filtrate (see Hofmeister, *J. Physiol.*, 1898, **23**, 130). The precipitate so obtained was dissolved in water and dialysed until free from sulphate, a little toluene being added to prevent putrefaction.

The albumen obtained in this way, however, did not behave like that employed by Findlay and Creighton, which was prepared from fresh eggs. Thus it was found impossible to work with solutions of greater concentration than 0·2 per cent., on account of the fact that coagulation occurred during the course of the solubility determination. We have not been able to ascertain the reason of the discrepant behaviour, and although we give the results obtained with this egg-albumen, we propose to regard them to some extent as provisional.

TABLE VI.—*Solubility of Carbon Dioxide in Solutions of Egg-albumen.*

(See also Fig. 3.)

Concentration: 0·105 gram of albumen in 100 c.c. of solution.

Density = 0·992.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 268 | 389 | 484 | 659 | 766 |
| Solubility ............ | 0·826 | 0·816 | 0·819 | 0·819 | 0·819 |
| Pressure ............ | 269 | 389 | 485 | 661 | 767 |
| Solubility ............ | 0·829 | 0·822 | 0·822 | 0·824 | 0·822 |

Concentration: 0·21 gram of albumen in 100 c.c. of solution.

Density = 0·995.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ............ | 269 | 387 | 483 | 664 | 772 |
| Solubility ............ | 0·844 | 0·827 | 0·823 | 0·826 | 0·824 |
| Pressure ............ | 268 | 388 | 484 | 663 | 769 |
| Solubility ............ | 0·843 | 0·829 | 0·824 | 0·823 | 0·824 |

### (*g*) *Silicic Acid.*

The solutions of silicic acid were prepared by adding excess of hydrochloric acid to solutions of sodium silicate, and dialysing the liquid. The concentration is expressed in terms of $SiO_2$.

TABLE VII.—*Solubility of Carbon Dioxide in Solutions of Silicic Acid.*

(See also Fig. 4.)

Concentration: 0·45 gram of $SiO_2$ in 100 c.c. of solution.

Density = 0·996.

| | | | | |
|---|---|---|---|---|
| Pressure ............... | 267 | 481 | 657 | 762 |
| Solubility ............... | 0·816 | 0·813 | 0·816 | 0·818 |

Concentration: 0·95 gram of $SiO_2$ in 100 c.c. of solution.

Density = 0·999.

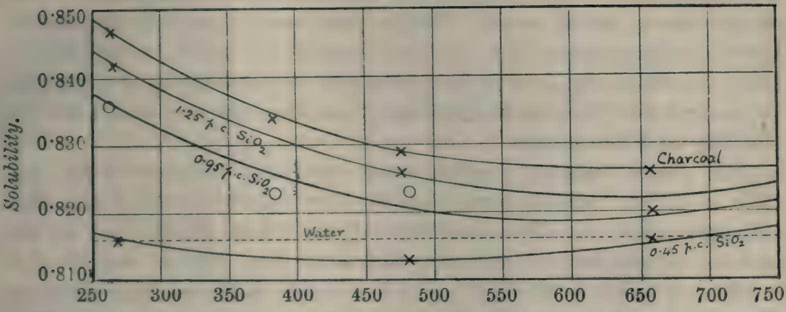
| | | | | | |
|---|---|---|---|---|---|
| Pressure ………… | 262 | 385 | 481 | 652 | 756 |
| Solubility ………… | 0·836 | 0·823 | 0·823 | 0·816 | 0·822 |

Concentration: 1·25 grams of $SiO_2$ in 100 c.c. of solution.

Density = 1·000.

| | | | | | |
|---|---|---|---|---|---|
| Pressure ………… | 265 | 384 | 477 | 657 | 765 |
| Solubility ………… | 0·842 | 0·826 | 0·826 | 0·820 | 0·824 |

FIG. 4.



*Pressure in mm.* Hg.
*Carbon dioxide and silicic acid.*
*Carbon dioxide and charcoal.*

### (*h*) *Suspensions of Silica and of Charcoal.*

Suspensions of silica gave values for the solubility which did not appreciably differ from those in pure water; with a suspension of charcoal, the following values were obtained (see also Fig. 4):

| | | | | | |
|---|---|---|---|---|---|
| Pressure ………… | 263 | 383 | 476 | 657 | 770 |
| Solubility ………… | 0·847 | 0·834 | 0·829 | 0·826 | 0·826 |

### *Discussion of Results.*

The results communicated in the preceding pages are found to be, on the whole, in harmony with those obtained at higher pressures by Findlay and Creighton. It is true that in the two series of determinations the actual values obtained for the solubility at atmospheric pressure are not in every case identical; but the discrepancies which are found are most probably to be accounted for by differences in the colloidal material employed. Such differences were marked in the case of solutions of egg-albumen, the preparation which we employed behaving very differently from that used by Findlay and Creighton. This was evidenced more especially by the ready coagulation of the albumen employed in this investigation. There appears another difference in the albumen used by us as compared with that employed in the previous investigation, namely, that its presence led to an increase in the solubility of carbon dioxide. We have not been able to decide as to the reason for this, but we trust to be able to do so later. It may be remarked, however, that the curves of solubility which we have obtained with albumen agree with those most generally met with in the case of colloids.

If the values of solubility, however, are not in some cases identical with those previously obtained, we have found that the general trend of the curves is the same. This is seen very clearly in the case of the solubility curve for carbon dioxide in solutions of starch (Fig. 2), which appears to be a straight line indicating a gradually increasing solubility with increasing pressure—as was found also by Findlay and Creighton.

This curve deserves remark more especially because of the fact that it differs rather conspicuously from that found with other colloidal solutions. Previous investigation had shown that in the case of a number of colloids, the solubility curve exhibited a minimum point or else fell, with increasing pressure, to a constant value. By the extension of the investigation to lower pressures, the fact is established that this is the general behaviour. With the single exception of starch solutions, the solubility of carbon dioxide in colloidal solutions is exceptionally high at low pressures and diminishes with increase of pressure either to a minimum or to a constant value. Even in the case of dilute solutions of dextrin in which the solubility of carbon dioxide was found, at higher pressures, to be independent of the pressure, we now find that at lower pressures there is the same increase in the solubility of carbon dioxide as is met with in the case of most other colloids. By an investigation of the solubility of nitrous oxide which is being carried out in this laboratory, we hope to be able to decide whether this form of solubility curve is connected with the chemical nature of the gas, or depends only on the colloidal character of the solutes. When that investigation is completed we hope to be in a better position to discuss the general form of the solubility curve. It is, however, apparent that the influence of colloids on the solubility of gases differs entirely from that of crystalloids. In the case of the latter, as was shown by Findlay and Shen (T., 1912, **101**, 1459), the solubility is in harmony with Henry's law; but in the case of the former, this was no longer found. The present extension of the investigation serves to confirm the unique and special behaviour of colloids with respect to gas solubility.

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# LXXII.—*A New Iron Bacterium.*

### By ERNEST MOORE MUMFORD.

HAVING been recently occupied with a short study of *Clamydothrix ochracea*, the author visited the Bridgewater canal tunnels at Worsley, Lancashire, with the view of examining the growths found there, since the waters of the tunnels and basin are strongly charged with iron, due to the entrance of the colliery pump water.

The basin into which the tunnels debouch is connected to the Bridgewater canal by two short sections of canal, and these, together with the tunnels and basin, are practically disused by traffic. From the two tunnels there issues in one case fresh, clear water without iron, but from the other—the deeper of the two—a yellow, opaque liquid, which colours the whole basin a deep ochre.

The walls of the basin, the woodwork, the grass and trees dipping into the water are covered with a reddish-yellow growth, which at first sight appears to be an aggregation of *Crenothrix* or *Cladothrix*, but it was found that, although the growth and precipitated material were composed of ferric hydroxide, the most careful search failed to reveal more than one or two strands of higher bacteria. Since these were totally insufficient in numbers to account for the mass of ferric hydroxide, a careful bacteriological dilution and plating was carried out which resulted in the isolation of the organism causing the growth, which was found to be a hitherto unnamed bacillus.

Obtained from these sources, the pure culture of the bacillus was used to investigate the specific action of the organism.

For want of a suitable name, the organism will be designated in this paper under its laboratory number, "Bacillus M. 7."

## *Description.*

| Growths on : | |
|---|---|
| Potato | Greenish-brown modules, rising high in the middle, spreading very slowly. |
| Milk | Coagulation, liquid becomes straw-coloured, no acidity. |
| Gelatin-peptone-bouillon | Liquefaction from surface and line of stab. Thick, white masses at the bottom of the liquid. |
| Peptone-bouillon | Opalescence, whitish strings appear. |
| Glucose in gelatin-peptone-bouillon | Shake culture—no gas. |
| Peptone-water | No indole reaction. |

Optimum temperature, 35—37°.

The organism is a facultative aerobe, and is of the average dimensions: 2·2 microns × 0·4 micron.

It is ciliated and exhibits a very varying motility; it occurs singly, and in short chains of three or four units.

The organism can form an endospore, but the majority of the bacilli under unfavourable conditions form a resistent involution form of varying shape, the general appearance of which is very similar to that presented by *Bacillus subtilis* under similar conditions.

An attenuated medium favours spore formation; a rich medium charged with the products of bacterial life favours involution forms.

### *Action of the Organism on Iron Solutions.*

Since the organism is a truly facultative one, the study of its action falls naturally into two sections, namely, (i) under aerobic conditions, and (ii) under anaerobic conditions.

#### (i) *Under Aerobic Conditions.*

In both ferrous and ferric solutions it was found necessary to supply a trace of nitrogen. This was done by the addition of 0·005 per cent. of peptone, since the entire absence of nitrogen prevents the growth of the organism.

(*a*) *Ferrous solutions.*—A solution of ferrous ammonium sulphate (0·05 per cent.) was used. Complete precipitation of ferric hydroxide took place in twenty-four to thirty-six hours at 37°. The reaction is essentially aerobic, and proceeds to completion, no iron remaining in solution.

(*b*) *Ferric solutions.*—A solution of ferric ammonium citrate (0·05 per cent.) was used. Complete precipitation took place in twenty-four hours at 37°. In this case also the action was complete, no iron remaining in solution.

With regard to the necessity of nitrogenous material in the media, it is the opinion of the author that this is necessary, not primarily for the metabolism of the organism, but to provide, through the metabolic action, highly basic amino-compounds which unite with the highly ionised acids freed by the precipitation of the metallic bases by the action of the organism, since a small amount of precipitation takes place in the absence of nitrogen, but the action quickly ceases.

In support of this view may be mentioned the oxidation of phenol by *Bacillus helvolus*, which action can proceed without any nitrogenous material in the media, since the acid formed is ionised only to a small degree. This is also in accordance with the effects of acid concentration in fermentations of cellulose.

### (ii) *Under Anaerobic Conditions.*

The organism will not precipitate ferric hydroxide from either ferrous or ferric solutions in presence or absence of peptone. If, however, ferric hydroxide is originally present, it is changed into bog ore. This can be shown with ferric hydroxide precipitated either biologically or chemically. In this case, also, a minute trace of nitrogen is essential, but increasing quantities accelerate the speed of reaction.

This the author regards as being in accordance with the previous observations with regard to nitrogen in relation to aerobic precipitation, since in this case, when there is no acid product formed, the organism can produce the change to completion in the absence of nitrogen outside its own content, but if nitrogen is added, it is used solely in establishing the protoplasm of new organisms, and therefore increases the speed of reaction, but does not affect the completeness. The reaction takes about fourteen days at 37°.

The medium taken consisted of 500 c.c. of tap water, in which were suspended 5 grams of ferric hydroxide chemically prepared, and in which were dissolved 2·5 grams of peptone. This was inoculated, exhausted, and allowed to ferment at 37° for eighteen days. The flask then contained a clear, straw-coloured liquid and a black solid. No gas was evolved. The product was filtered and examined.

The residue, which was black, was dried and analysed. (Found, $FeO = 9·00$; $Fe_2O(OH)_4 = 91·00$ per cent.) It consisted therefore of bog ore.

The filtrate was a yellow liquid, neutral towards litmus, but basic to acids, which on evaporation in a vacuum gave a yellowish-white solid having an unpleasant odour. On esterification, this solid yielded a mixture of the esters of amino-acids. If this filtrate is added to solutions containing iron (composed as before), precipitation takes place under certain conditions.

This naturally suggests that the organism produces an enzyme which is the cause of these reactions, and it was therefore necessary to determine if an enzyme could be separated and used to produce the effects associated above with the living organisms. It was found that if a solution in which the organism was growing freely was filtered through a Chamberland candle, the filtrate had the power of producing the reactions associated with that living organism.

This property is extended to the filtrate irrespective of the presence of iron in the medium. It is produced only in minute quantities in the absence of nitrogen, but in order to secure the most reactive enzyme, the latter was produced by the action of the organism on peptone water.

### *Isolation of the Enzyme.*

Peptone water, containing 10 grams per litre, is prepared and sterilised in the usual way. It is then inoculated, incubated at 37° for twenty-four hours, and filtered through a Chamberland candle. Thymol is added to the solution to prevent further bacteriological action.

The most reactive enzyme is obtained after twenty-four hours' incubation. After a longer time it becomes weaker and disappears, being probably broken up by the bacteria as the pabulum becomes exhausted.

The enzyme is not destroyed by boiling or by evaporation in a vacuum, but is destroyed on being kept for forty-eight hours.

*Reactions of the Enzyme.*—The filtrate is not precipitated by picric acid, alcohol, ammonium sulphate (saturated solution), or sodium phosphotungstate (saturated solution), but is precipitated by Millon's reagent.

A white solid is obtained by evaporation in a vacuum. This white solid was, with the view of an approximate identification, esterified. On distillation and fractionation, several esters were separated, which were esters of the amino-acids usually associated with the partial, bacterial degradation of complex proteins. Some acids containing sulphur were also present.

### *Experiments carried out with the Filtrate containing the Enzyme.*

Qualitative tests showed that the filtrate was able to produce the characteristic actions of the organism.

Solutions of ferrous salts are oxidised and precipitated; solutions of ferric salts are precipitated.

Analysis of the precipitate showed it to consist of ferric hydroxide in all cases. With the view of determining the optimum temperature of the enzyme, the simple precipitating reaction was studied.

Solutions of 10 c.c. of 0·05 per cent. of ferric ammonium citrate and 0·5 c.c. of the filtrate were used with the following result:

| Precipitation at | Time. |
|---|---|
| 37° | 1·5— 2 hours |
| 60 | 20—25 minutes |
| 70 | 10—15 ,, |
| 80 | 20—25 ,, |

On boiling, partial precipitation took place in five to six minutes. If 1, 5, or 10 c.c. of the enzyme are taken, the speed is not increased.

The optimum temperature of the enzyme thus appears to be 70°.

Experiment has also shown that when the ratio between the filtrate and the iron solution varies between one part of filtrate and one part of iron solution, and one part of filtrate and fifty parts of iron solution, the speed or completeness of the precipitation is not appreciably affected. The precipitate in all cases is ferric hydroxide.

*Character of Enzyme.*—The filtrate was examined in the above manner after having been treated thus: (i) Fresh filtrate; (ii) filtrate kept overnight; (iii) filtrate boiled; and (iv) filtrate evaporated to dryness and extracted with water.

| | | |
|---|---|---|
| i. | Reactions as above ........................ | Active |
| ii. | No precipitation ........................... | Inactive |
| iii. | Reaction as (i), but slower ............... | Active |
| iv. | Reaction as (i), but very slow ..... ... | Active |

The boiled solution only decomposes and becomes inactive in the course of several days.

*Basicity.*

*Active.*—50 c.c. fresh filtrate required 4·2 c.c. $N/10$-acid.

*Inactive.*—50 c.c. (kept overnight) required 7·5 c.c. $N/10$-acid.

*Active.*—50 c.c. boiled liquid required 12·8 c.c. $N/10$-acid.

There is therefore no apparent relation between basicity and enzymatic power. The fresh solution is more active than the boiled solution, although the latter precipitates at 70° in twenty to twenty-five minutes.

With regard to the mechanism of precipitation, the chief points may be summarised as follows:

The precipitation is produced by a crystalloid product formed by the organism from nitrogenous matter.

The optimum temperature of this crystalloid product, known as the "enzyme," is 70°.

It has not been found possible to produce the enzyme in appreciable quantity from media containing no nitrogen.

Starch and dextrose solutions in the presence of salts do not yield the enzyme in any appreciable quantity.

Therefore the organism, although living and reproducing in certain media, cannot produce the precipitating product except under certain conditions.

Since this is so this substance will depend for its nomenclature on the definition of an enzyme. Two broad conceptions of an enzyme are possible, namely, a product of the normal metabolism of the organism, and a product of the metabolism of the organism dependent for its formation on the nature of the surrounding medium.

This enzymatic substance falls under the second definition, but not under the first, so that this precipitating agent must be described, according to the definition accepted, in the one case as a chemical precipitant produced by the organism under certain conditions, in the other case as a true enzyme.

### *Summary.*

The bacillus is a true facultative organism, preferably an aerobe, and exercises a specific action on iron solutions.

The action of the bacillus on iron solution appears to proceed in two stages, in which the aerobic and anaerobic actions appear to be symbiotic, at any rate in nature.

The aerobic action is to precipitate ferric hydroxide from iron solutions, whilst the anaerobic action is to transform the ferric hydroxide thus precipitated to bog ore with partial reduction of the iron to a ferrous state.

To this organism are probably due the deposits of bog ore hitherto associated with the higher bacteria, since the latter have not the facultative power necessary to dehydrate and reduce the ferric hydroxide to bog ore.

I am indebted to Dr. G. J. Fowler for valuable suggestions and criticisms in the course of the above research.

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## LXXIII.—*Gossypetin.*

By ARTHUR GEORGE PERKIN.

GOSSYPETIN, a colouring matter of Indian cotton flowers, *Gossypium herbaceum* (T., 1899, **75**, 826), also present in the Egyptian variety (*ibid.*, 1909, **95**, 2181), and in the flowers of the *Hibiscus sabdariffa* (*ibid.*, 1909, **95**, 1855), has hitherto only been subjected to cursory examination. Originally considered to possess the formula $C_{16}H_{12}O_8$, it was subsequently shown that this is more probably $C_{15}H_{10}O_8$, the earlier preparation having apparently contained a trace of quercetin, which in appearance and many of its properties it closely resembles. Gossypetin forms oxonium salts with mineral acids, its general reactions indeed possessing a flavonol character, and that it might reasonably be expected to possess such a constitution receives further support from its formula and the fact that it contains six hydroxyl groups. With the object of obtaining some more definite clue to its constitution, application was made to India for a large supply of the flowers, and my thanks are due to Mr. T. H. Burkill, Reporter on Economic Products to the Government of India, and to Mr. D. H. Hooper, the Officiating Reporter, for their liberal response to this request. The author again is indebted to Mr. H. M. Leake, Economic Botanist to the Government of the United Provinces of Agra and Oudh, for a similar favour, and also for certain special varieties of the flower which he himself had more recently investigated (*Proc. Roy. Soc.*, 1911, *B*, **83**, 447). For the preparation of the colouring matter a small quantity of the material was extracted in the laboratory, but an alcoholic extract and in part an aqueous extract of the main bulk were very kindly prepared by Messrs. Hirst, Brooke, and Hirst, of Leeds.

## EXPERIMENTAL.

The alcoholic extract in quantities of 500 grams was added to 6 litres of hot water and boiled with 240 c.c. of hydrochloric acid (33 per cent.) for three hours. The tarry matter which had then separated was removed by filtration, and the yellow, semicrystalline product which was deposited from the clear liquid on cooling was collected and roughly purified by crystallisation from dilute alcohol. The yield was 32 grams. When operating with the aqueous extract of the flowers the process was of a more tedious nature, for this, when digested with boiling dilute acid, gave a voluminous, reddish-brown precipitate, consisting of a mixture of the colouring matter with much phlobaphen, and it thus appeared certain that these flowers contain as mineral salt a phlobatannin, readily soluble in water, although insoluble in alcohol. The product was collected, dried, and extracted with boiling alcohol, which dissolved the colouring matter and but little of the phlobaphen, the solution evaporated to a small bulk, cautiously diluted with boiling water, and the brownish-yellow deposit again crystallised from dilute alcohol.

When isolated by either of these methods the crude substance, in addition to non-tinctorial impurity, contained at least two colouring matters, which could be separated by the fractional crystallisation of their mixed acetyl derivatives. Thirty grams of substance, 120 c.c. of acetic anhydride, and fifty drops of pyridine were boiled for one hour, and after keeping overnight the crystals which had separated were collected (the filtrate *A* being reserved for examination), and weighed 26 grams. On heating, this product sintered slightly at 190—196°, more markedly at 210°, and was completely melted at 226—228°. A further digestion for half an hour with 50 c.c. of boiling acetic anhydride was now resorted to, and the substance finally crystallised a third time from the same solvent. The crystals now weighed approximately 16 grams, and melted fairly sharply at 228—230°. In certain instances the last treatment with the anhydride was dispensed with, and the acetyl compound crystallised from a mixture of solvent naphtha and nitrobenzene. Finally, it was hydrolysed with sulphuric acid in the presence of acetic acid in the ordinary manner.

Found: $C_{15}H_{10}O_8=55\cdot59$.

$C_{15}H_4O_8(Ac)_6$ requires $C_{15}H_{10}O_8=55\cdot76$ per cent.

An analysis of the gossypetin dried at 160° gave the following result.

Found: $C=56\cdot70$; $H=3\cdot28$.

$C_{15}H_{10}O_8$ requires $C=56\cdot60$; $H=3\cdot14$ per cent.

From the acetic anhydride mother liquors by evaporation and subsequent dilution with alcohol acetylated products of indefinite melting point were isolated, which, when fractionated, gave a further amount of acetylgossypetin. By these methods approximately 80 grams of pure gossypetin were obtained for experiment.

It has been shown (T., 1909, **95**, 2181) that the Egyptian cotton flowers yield in addition to gossypetin a considerable amount of quercetin, and it was to be anticipated that the Indian variety would give a similar result. This proved to be the case, for an examination of the acetic anhydride mother liquor (*A*) revealed the presence of acetylquercetin, and, indeed, on long keeping this was frequently deposited in an almost pure condition, and could be obtained pure by crystallisation from a mixture of alcohol and acetic acid. It melted at 193—195°, and on hydrolysis gave quercetin, which was recognised by its well known properties. (Found, $C=58\cdot62$; $H=3\cdot84$. $C_{25}H_{20}O_{12}$ requires $C=58\cdot59$; $H=3\cdot90$ per cent.)

Owing to the persistent sintering which occurs when the partly purified acetylgossypetin was heated to about 210°, a search for the isomeric acetylquercetagetin (T., 1913, **103**, 212), which melts at 210—211°, was carried out, but without result. It is, however, considered still possible that in addition to quercetin and gossypetin a small amount of a third colouring matter is yielded by these flowers.

When fused with alkali gossypetin gives protocatechuic acid (*loc. cit.*), and this can be produced in abundance by dissolving the colouring matter in cold 50 per cent. aqueous potassium hydroxide, and allowing the solution to remain exposed to air for twenty-four hours with occasional shaking. It has not yet, however, been found possible to determine the character of the second nucleus present in this colouring matter by these methods.

*Methylation.*—Gossypetin (8 grams) in 90 c.c. of methyl alcohol was treated with 50 c.c. of methyl iodide, and to the boiling mixture a solution of 20 grams of potassium hydroxide in methyl alcohol was slowly added during two days. At the end of the first day it was necessary that when kept overnight air should be excluded so far as possible from the product, otherwise a considerable oxidation took place, with the formation of a blue-coloured potassium salt. The mixture, after being evaporated to a small bulk, was poured into ether (*A*), and on adding water a fine, almost colourless, crystalline precipitate separated in the aqueous layer. This was collected (3·8 grams), and when recrystallised from alcohol possessed a pale yellow appearance, but by the use of alcohol containing a little alcoholic potassium hydroxide was readily obtained in a colourless condition.

Found: C=62·44; H=5·52; $CH_3$=22·33.

$C_{21}H_{22}O_8$ requires C=62·68; H=5·47; $CH_3$=22·38 per cent.

*Gossypetin hexamethyl ether*, $C_{15}H_4O_2(OMe)_6$, separates as a rule in colourless needles, although occasionally in the prismatic form, and on one occasion the needles which had separated on long keeping in contact with the alcohol gradually changed into the latter modification. It is sparingly soluble in cold alcohol, and melts at 170—172°.

The ethereal liquid (*A*) on evaporation yielded a small amount of crystalline substance; this separated from alcohol in yellow needles, but insufficient for satisfactory examination.

In order to study the products of the hydrolysis of the hexamethyl ether, to a solution of 2·8 grams of potassium hydroxide in 14 c.c. of 80 per cent. alcohol 1·4 grams of the substance were added, and the mixture boiled for six hours. After removal of the alcohol the residue was dissolved in a little water, and treated with carbon dioxide, which caused the separation of a colourless, crystalline precipitate. This was collected, a further amount being isolated from the aqueous liquid by means of ether. It was purified by recrystallisation from alcohol.

Found: C=56·02; H=6·08; $CH_3$=23·53.

$C_{12}H_{16}O_6$ requires C=56·24; H=6·25; $CH_3$=23·43 per cent.

*Gossypitol tetramethyl ether*, the name proposed for this substance, forms long, colourless needles, melting at 115—116°, and sparingly soluble in cold alcohol.

The bicarbonate solution when neutralised with acid gave a colourless precipitate, which, on crystallisation from dilute alcohol, separated in needles melting at 180—182°, and consisted of veratric acid.

*Ethylation.*—The yield of substance obtained by methylating gossypetin being somewhat poor, the ethylation of the colouring matter was now studied. Ten grams of gossypetin in 120 c.c. of absolute alcohol and 60 grams of ethyl iodide were boiled with addition of 25 grams of potassium hydroxide in alcohol a little at a time during two days, care being taken as in the methylation process to avoid admission of air. At the end of the operation the mixture was filtered, the filtrate evaporated to a small bulk, and poured into much ether whilst hot, as otherwise it gelatinises. The solution, which yielded practically nothing to dilute alkali, on evaporation gradually deposited needles, which were collected (6·35 grams) and washed with a little ether. By crystallisation from very dilute alcoholic potassium hydroxide a trace of a yellow compound was removed.

Found: C=66·37; H=7·20; Et=35·85.
$C_{27}H_{34}O_8$ requires C=66·66; H=7·00; Et=35·80 per cent.

*Gossypetin hexaethyl ether*, $C_{15}H_4O_2(OEt)_6$, is colourless, sparingly soluble in cold alcohol, and melts at 144—146°.

The hydrolysis of this compound (7·1 grams) was carried out as with the methyl derivative, employing the same proportions of alcohol and alkali. The product after being evaporated to dryness was dissolved in water, and treated with carbon dioxide, yielding 3·84 grams of a crystalline precipitate, whereas 0·2 gram of the same product was isolated from the aqueous liquid by means of ether. It was purified by crystallisation from alcohol.

Found: C=61·46; H=7·72; Et=36·25.
$C_{16}H_{24}O_6$ requires C=61·53; H=7·69; Et=37·17 per cent.

*Gossypitol tetraethyl ether* consists of colourless needles melting at 110—111°, sparingly soluble in cold alcohol. The mother liquors obtained during the purification of this compound contained a small amount of a more soluble substance, which remained after evaporation as a viscid mass.

The bicarbonate solution when neutralised with acid gave a crystalline precipitate, which was collected (2·892 grams) and recrystallised from dilute alcohol. (Found, C=62·83; H=6·70. $C_{11}H_{14}O_4$ requires C=62·85; H=6·66 per cent.)

It was obtained in long, colourless needles melting at 166—167°, and evidently consisted of protocatechuic acid diethyl ether.

As was anticipated, gossypitol tetraethyl ether proved to contain a carbonyl group, and an oxime could be readily prepared from it by Lapworth and Steele's method (T., 1911, **99**, 1884). Half a gram of the ketone, 0·5 gram of anhydrous sodium acetate, 0·2 gram of hydroxylamine hydrochloride, and 25 c.c. of alcohol were boiled for five hours, the main bulk of the alcohol then distilled off, and the residue treated with hot water. The crystals which separated were collected, washed with hot carbon disulphide, and recrystallised from benzene, from which they separated in long, colourless needles, melting at 127—129°.

Found: C=58·59; H=7·77; N=4·31; Et=34·95.

$C_{16}H_{25}O_6N$ requires C=58·65; H=7·64; N=4·28; Et=35·17 per cent.

With the object of obtaining some further insight into its constitution, gossypitol tetraethyl ether, 3·84 grams dissolved in a solution of 2 grams of potassium hydroxide in 384 c.c. of water, was gradually treated at 5° with 2 grams of potassium permanganate in 200 c.c. of water. Oxidation readily took place, and at the end of the operation the mixture was heated on the steam-bath, filtered, and the clear liquid evaporated to a small bulk. By treatment with carbon dioxide and extraction with ether, 0·75 gram of the unattacked ketone was recovered. The solution when now neutralised with acid became cloudy, and yielded to ether a pale brown, viscid substance; this was extracted with boiling benzene, the liquid evaporated, and the crystals which had separated after keeping for some days were collected. The yellow, crystalline powder (0·27 gram) was digested with some quantity of boiling water, whereby a trace of an orange-coloured, resinous impurity remained undissolved; and on cooling pale yellow needles were deposited (*A*), whereas a further quantity was obtained on concentrating the liquid (*B*). Only 0·175 gram of this compound was available for analysis:

0·0981 gave 0·2016 $CO_2$ and 0·0546 $H_2O$. C=56·05; H=6·18; Et=28·83.

0·0720 gave 0·1682 AgI.

$C_{14}H_{18}O_6$ requires C=56·37; H=6·04; Et=29·19 per cent.

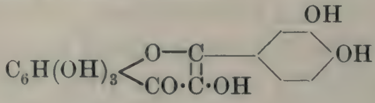
This acid, for which the name *gossypetonic acid* is suggested, although here described as a pale yellow substance, is probably in reality colourless, but sufficient material was not available to ascertain if this was certainly the case. Both fractions *A* and *B* melted at 154—155°, with evolution of gas.

As gossypitol tetraethyl ether, $C_{16}H_{24}O_6$, is soluble in potassium hydroxide solution it contains a free hydroxyl group, and as it yields an oxime, and further possesses four ethoxy-groups, all the oxygen atoms are accounted for. There is accordingly little doubt, therefore, that its constitution is as follows (I):

$$HO\cdot C_6H(OEt)_3\cdot CO\cdot CH_2\cdot OEt \qquad HO\cdot C_6H(OEt)_3\cdot CO\cdot CO_2H$$

(I.) (II.)

and, again, the analytical figures of gossypetonic acid harmonise with this view, as they are in agreement with those required by a *hydroxytriethoxybenzeneglyoxylic acid* (compare Herzig, *Monatsh.*, 1891, **12**, 187). The results, therefore, of the hydrolysis of gossypetin hexaethyl ether with alcoholic potassium hydroxide suggest that it possesses the flavonol constitution (III), as, indeed, its general properties also indicate.



(III.)

A remarkable resemblance is thus to be observed between gossypetin and quercetagetin (T., 1913, **103**, 219), in that both are hexahydroxyflavones, containing in each case tetrahydroxybenzene and catechol nuclei.

The melting point of gossypetin about which some uncertainty existed owing to the blackening of the tube, and which was considered (*loc. cit.*) to be about 300°, is now found to be in reality 311—313°. For the reason indicated the exact point is not apparent, and to be certain that fusion had occurred, the breaking of the tube was necessary.

### *An Oxidation Product of Gossypetin.*

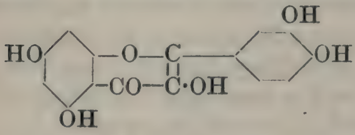
As previously stated (*loc. cit.*), gossypetin is readily susceptible to oxidation in alkaline solution, the liquid passing through brown, orange, and green to deep blue, and it was interesting to determine the cause of this colour change. The deep blue solution on acidification becomes red, and if concentrated deposits a reddish-brown precipitate, which on gentle warming usually becomes crystalline. That this reaction is not deep-seated appears evident, for when the acid mixture is treated with sodium hydrogen sulphite solution a reconversion into yellow gossypetin quickly takes place, and the re-oxidation of this with air and subsequent reduction can be performed *ad libitum*. A second method consists in adding alcoholic potassium hydroxide to an alcoholic solution of the colouring matter, the precipitated potassium salt rapidly becoming blue-coloured, and this is collected, dissolved in water, and the clear blue liquid treated with acid. Other oxidising agents were experimented with, and eventually *p*-benzoquinone was selected as being most convenient. A solution of 0·5 gram of gossypetin dissolved in 8 c.c. of absolute alcohol was treated when cold with 0·2 gram of *p*-benzoquinone with agitation, causing the development of a deep reddish-brown coloration. On keeping for a few minutes minute crystals commenced to separate, and the mixture was then heated to 50° until a semi-solid mass was obtained. The product, after being collected and washed with boiling alcohol, weighed 0·457 gram, and in other experiments the yield averaged 90 per cent.

Found: C=56·90, 57·02; H=2·74, 2·79.
$C_{15}H_8O_8$ requires C=56·96; H=2·53 per cent.

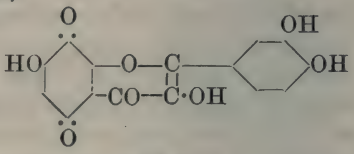
*Gossypitone*, the name proposed for this substance, consists of microscopic needles having a dull red or maroon colour, and, indeed, closely resembles amorphous phosphorus in appearance. It is insoluble in cold water, boiling alcohol, or nitrobenzene, sparingly soluble in boiling water, but readily so in pyridine or quinoline, although apparently it cannot be crystallised from the two latter solvents. Dilute alkalis dissolve it with a pure blue coloration, and when acidified a red liquid is produced in very dilute solutions, but a solution of the dried substance in concentrated sulphuric acid is dull brown. In order to reconvert the gossypitone into gossypetin, 0·8 gram of the former in 200 c.c. of boiling water was treated with 10 c.c. of concentrated sodium hydrogen sulphite solution. The yellow solution on acidification deposited 0·765 gram of minute needles, which on acetylation gave acetylgossypetin, melting at 228—230°. (Found: C=56·90; H=4·06. $C_{15}H_4O_8(Ac)_6$ requires C=56·84; H=3·86 per cent.)

The latter experiment indicates that gossypitone is not a quinhydrone, but a quinone, and the fact also that it is reduced in the cold by phenylhydrazine with brisk evolution of nitrogen fully supports this view. The behaviour of gossypetin is indeed similar to that of excoecarin (T., 1902, **81**, 214), $C_{13}H_{12}O_5$, a colouring matter of green ebony, which with bromine and apparently also by means of *p*-benzoquinone yields the green excoecarone, $C_{13}H_{10}O_5$, to which the tint of green ebony on keeping is no doubt due. With sulphurous acid it is at once reconverted into excoecarin, and as the latter contains a quinol or toluquinol nucleus, excoecarone is thus probably a paraquinone.

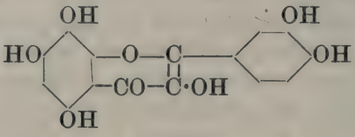
Wheldale (*Report to the Evolution Committee of the Royal Society*, 1909, **5**, 1), as a result of experiments with *Antirrhinum* *majus*, has made the interesting suggestion that anthocyanin * (in this case the magenta anthocyanic pigment) "may be regarded as an oxidation product of a chromogen in nature allied to the series of flavone colouring matters; the oxidation is brought about probably through the agency of an oxydase." Evidence for this hypothesis is derived by this author from results obtained in cross-breeding with varieties of *Antirrhinum majus*, and is also given in other papers; moreover, in the *Biochemical Journal* (1913, **7**, 85) the matter is further elaborated, and it is considered that anthocyanin includes many substances, "having in general similar properties, but differing among themselves as regards constitution," and "would occur as glucosides." Nierenstein and Wheldale (*Ber.*, 1911, **44**, 3487), again, have oxidised quercetin (I) with chromic acid, and obtained quercetone, a red substance soluble in alkali with a blue colour, for which the constitution (II) is suggested. This latter compound, considered by these authors to consist possibly of an anthocyanin by simultaneous acetylation and reduction, yields the acetyl compound of the flavonol (III):



(I.)



(II.)



(III.)

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* Anthocyanin, or cyanin, according to Frémy and Cloez (*J. pr. Chem.*, 1854, **62**, 629), is an amorphous, blue powder present in flowers. With acids it gives a red, with alkalis a green, colour, and is decolorised by reducing agents, though the blue returns on exposure to air. These authors consider that the red colour of flowers is this compound, reddened by the acidity of vegetable juice. On the other hand, anthocyanin appears to be generally regarded by botanists as the red colour of flowers turning blue with alkali, although Weigert (compare Wheldale, *Proc. Roy. Soc.*, 1909, *B*, **81**, 44) again describes two classes of anthocyanin, "weinrot" and "rübenrot," the former giving, with basic lead acetate, bluish-green, and the latter, red precipitates. Wheldale (*Report to Evolution Committee*, *loc. cit.*) also includes, among the anthocyanines, a "pigment" present in the "Rose Doré" variety of *Antirrhinum majus*, which is not turned blue by alkali, so, consequently, it would appear that the term "anthocyanin" refers to the red colouring matter of any flower. According to Molisch (*Bot. Zeit.*, 1905), anthocyanin frequently exists in the cell in a crystalline condition, and Wheldale has isolated, from a variety of the *Antirrhinum majus*, a crystalline magenta "pigment" which decomposes when heated to 340° (*Biochem. J.*, *loc. cit.*).

The properties assigned to quercetone resemble those possessed by gossypitone, but although little doubt appears to exist that they should be closely allied, the fact that the former gives with concentrated sulphuric acid a red solution is proof that they cannot be identical. Moreover, the flavonol (III) is not gossypetin, for it melts at 352—359°, and its hexamethyl ether at 147—149°.

That the anthocyanin of certain flowers arises from the production of a flavone-quinone or of its glucoside seems plausible, although such being the case it appears open to conjecture whether the quinone, as in the above example, is derived directly from the quercetin, or whether the quinol itself (or other flavone readily susceptible to quinonoid transformation) is synthesised in the plant without an intermediate quercetin stage. Flavone colouring matters rarely exist singly in flowers, although frequently owing to its small amount the presence of the second constituent of this class is not always apparent. Purified preparations of quercetin and other flavonols when exposed to air frequently develop a more or less green tint, and special mention in this respect may be made of rutin prepared by the usual methods, either from rose petals or the flower buds of *Sophora japonica.* Such a behaviour indicates the presence of a trace of an otherwise unsuspected colouring matter, which is readily oxidisable, and possibly, therefore, the parent of an anthocyanin. Although experiments are incomplete, it is probable that *p*-benzoquinone in alcoholic solution will prove a useful reagent for the detection of traces of such compounds in flavone preparations, by the development of a reddish-brown tint, which will be pale or otherwise according to circumstances. Observations hitherto carried out are promising in this respect, and indicate that with pure flavonols no reaction of this character occurs.

Gossypitone possesses strong dyeing properties, and gives the following shades with mordanted woollen cloth:

| Chromium. | Aluminium. | Tin. | Iron. |
|---|---|---|---|
| Dull brown. | Orange-brown.* | Orange-red. | Deep olive. |

* On mordanted calico the shade is greenish-brown.

These, it is interesting to note, are identical with those given in these circumstances by gossypetin itself, and it is accordingly evident that during this dyeing operation oxidation of the latter to gossypitone takes place. The dyeing experiments with gossypetin are described in a previous communication (*loc. cit.*).

Although the flowers of the ordinary Indian cotton plant are yellow, other varieties are to be met with, such as those of the *G. arboreum*, which are of a red colour. In a lengthy paper, "Studies on Indian Cotton" (*Journal of Genetics*, 1911, **1**, 203), by H. M. Leake, special reference to this anthocyanic pigment occurs, and it is pointed out that in plants of the type *G. arboreum* and *G. sanguineum* its presence communicates an intense red to the entire plant (stem, leaves, and flowers). Owing to the kindness of Mr. Leake, a supply of these red petals has been available for examination, and there can be no doubt that these also contain gossypetin as glucoside. The fact that gossypetin can be readily converted into red gossypitone provides at first sight a simple explanation of the origin of the red colour of this variety of flower, but although in a sense this may be partly correct, it is doubtful whether gossypitone exists as such, at least in the freshly gathered petal.

A point of importance in regard to anthocyanin, and to which botanists do not appear to have called attention, is the fact, borne out by numerous dyeings in this laboratory with freshly gathered flowers, that towards mordanted fabrics it behaves as a fugitive green or greenish-blue colouring matter.* Most probably it is a blue dyestuff, the shade in these instances being modified by the presence of flavone glucosides, although apparently owing to the very elastic definition applied by botanists to these products a hard and fast rule on this point is impossible.

Employing mordanted calico, air-dried red cotton-flower petals, however, give the anticipated green "anthocyanic" shade, or at least a much greener shade than that produced by the yellow variety, whereas in case free gossypitone had been present a brownish-yellow shade should have resulted. That anthocyanins, as indeed Wheldale (*loc. cit.*) has suggested, are glucosides seems certain owing to their ready solubility, and an experiment was now carried out to determine if gossypitone could be prepared in a similar form.

The result of a preliminary investigation of the Indian cotton flowers has shown that they contain the gossypetin or at least part of it in the form of a glucoside sparingly soluble in hot water. This compound gives an acetyl compound melting at 239—242°, but whether it is in reality the gossypitrin formerly isolated from the Egyptian variety or a modification of it has not yet been decided. A solution of this substance in dilute alcohol when treated with a little *p*-benzoquinone in the cold, became brownish-red, and gradually deposited a gelatinous, maroon-coloured precipitate similar to gossypitone. On heating the mixture the substance became crystalline, and when collected, washed with alcohol, and dried formed a glistening mass of reddish-violet needles. Although at first sight it seemed evident that here was a glucoside of gossypitone, this is by no means certain in that its alkaline solutions are not blue but orange-yellow. Very interesting, however, are the dyeing results given by this glucoside; for employing mordanted calico it yields bright green shades, which are the cumulative effect of a blue and yellow colouring matter, into which it appears to be converted by the action of the boiling water. Owing to the fugitive character of the blue dye, this gradually disappeared on exposure to the laboratory atmosphere for a few days, a yellow pattern thus resulting. These preliminary results are here given because as the preparation of the gossypetin glucoside is laborious the explanation of this reaction must occupy a considerable time.

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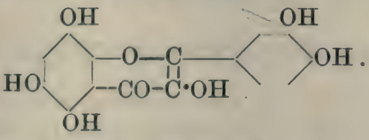
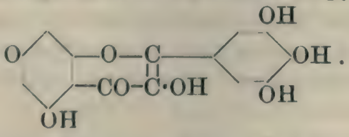
* Nierenstein and Wheldale have not described the dyeing properties of their quercetone.

Until a definite knowledge of the tetrahydroxybenzene nucleus present in gossypetin has been obtained, the position of the hydroxyl groups in this portion of the molecule can only be conjectured. Existing as it does side by side with quercetin, it seems natural to consider that gossypetin is a hydroxyquercetin. Again, should gossypitone be a *p*-quinone, the constitution of gossypetin will be the same as that which Nierenstein and Wheldale have suggested for the flavonol (*loc. cit.*) which they obtained from quercetone, but the descriptions of the two compounds are not in agreement. On the assumption of the necessity for a quinol nucleus in gossypetin, a second constitution already referred to in connexion with quercetagetin (*loc. cit.*) is possible:



On the other hand, it suggests itself as not unreasonable that gossypitone may eventually prove to be an orthoquinone*; thus the presence of a pyrogallol grouping in the nucleus in question is very possible, and, if so, would account for the ready oxidation of the alkali salts of gossypetin. Interesting in this respect is the fact recently ascertained that by means of alcoholic *p*-benzoquinone solution pyrogallol gives the compound $C_6H_4O_3$, possibly hydroxy-*o*-benzoquinone, formerly obtained with *iso*amyl nitrite (T., 1906, **89**, 802). Myricetin again, which possesses a pyrogallol nucleus,



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* The reactions of anthocyanin or cyanin given by Frémy and Cloez (*loc. cit.*) suggest that this is very probably an orthoquinone.

behaves very similarly to gossypetin when its alkaline solution is exposed to air (T., 1896, **69**, 1287), and preliminary experiments have shown that if this is carried to the blue stage, on acidification a reddish-brown precipitate, apparently of a similar nature to gossypitone and reducible with sulphurous acid, is obtained. Alkaline oxidation with myricetin is, however, difficult to control, as a change from the blue to a reddish-violet stage rapidly occurs, even if the salt is prepared in alcoholic solution, and it is anticipated that the reaction may be troublesome to elucidate. With alcoholic *p*-benzoquinone also myricetin yields a bright scarlet liquid (but no deposit as in the case of gossypetin), and these colour changes, originating in its pyrogallol grouping, may reasonably be inferred to have an orthoquinonoid explanation.

A further investigation of these points is now in progress.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

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## LXXIV.—*Studies in the Camphane Series. Part XXXIV. Configuration of the Eight Oximino-derivatives of Camphorquinone.*

By MARTIN ONSLOW FORSTER.

BENZIL is the model case of a symmetrical α-diketone in which the configuration of each oximino-derivative has been established. This is due to Beckmann and Köster (*Annalen*, 1893, **274**, 1) who, by following the course of a Beckmann transformation applied to the two monoximes and three dioximes, drew conclusions regarding the spacial disposition of the hydroxyl groups relative to the other parts of the molecule.

The discovery of *iso*nitrosoepicamphor in two modifications, constituting the third and fourth monoximes of camphorquinone (T., 1912, **101**, 1340), thereby completing the series of eight oximino-derivatives from that diketone, invited an attempt to establish the configuration of these materials on the lines of the Hantzsch-Werner hypothesis, because they present the only recorded case in which all the possible derivatives of an unsymmetrical α-diketone have been isolated.

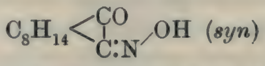
Owing to the stability of the camphor nucleus, the method of Beckmann and Köster can be applied in only modified form to the monoximes, and in the case of the dioximes it has been necessary to rely on arguments which, although perhaps appearing less conclusive at first, certainly have the advantage of depending on less drastic transformations. Briefly stated, this part of the investigation has resolved itself into an inquiry as to the identity of the dioximes arising by the action of hydroxylamine on each monoxime, and then, by a process of elimination based on preliminary knowledge of the configuration of the monoximes themselves, deciding the disposition of the hydroxyl groups in the four dioximes. For this purpose it has appeared desirable to repeat much of the earlier work on the dioximes (T., 1903, **83**, 514), and by improving the methods of separating these, to determine with greater certainty their relationship to the monoximes.

Beyond giving the following table, in which details regarding more highly purified materials are slightly amended, it is not necessary to recapitulate the information which has been published from time to time concerning the eight oximino-derivatives of camphorquinone, the history of these compounds having been summarised recently:

| | | $[\alpha]_D$. | |
|---|---|---|---|
| | M. p. | Chloroform. | 2 per cent. NaOH. |
| *iso*Nitrosocamphor (unstable)......... | 114° | 172·9° | 275·3° |
| ,, (stable) ......... | 152 | 197·0 | 288·0 |
| *iso*Nitrosoepicamphor (unstable) ... | 137 | −179·4 | −278·5 |
| ,, (stable) ...... | 170 | −200·1 | −422·0 |
| Camphorquinone α-dioxime ......... | 201 | −51·7 | −103·8 |
| ,, β-dioxime ......... | 248 | — | −24·5 |
| ,, γ-dioxime ......... | 136 | 16·4 | 14·3 |
| ,, δ-dioxime ......... | 194 | 52·8 | 87·0 |

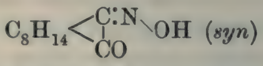
It must be recalled, however, that the configuration of the two modifications of *iso*nitrosocamphor has been established (T., 1905, **87**, 232), and the recognition of the stable and unstable forms as *syn*- and *anti*-modifications respectively is the starting point of the present inquiry.

On comparing these isomerides with the third and fourth monoximes of camphorquinone, a similar relationship for the latter suggests itself. The unstable, more readily fusible, more freely soluble, and less optically active *iso*nitrosoepicamphor corresponds exactly with the *anti*-monoxime represented by the unstable form of *iso*nitrosocamphor, and most probably has, therefore, the *anti*-configuration. This diagnosis is strengthened by the effect of magnesium methyl iodide examined by Dr. Spinner, who has found that the behaviour of unstable *iso*nitrosoepicamphor is strictly analogous to that of unstable *iso*nitrosocamphor, there being produced a hydroxy-oxime which does not yield the anhydride with hot alkali, whilst the stable *iso*nitrosoepicamphor gives a mixture of the hydroxy-oxime with the anhydride. Moreover, whilst the unstable *iso*nitrosoepicamphor may be extracted unchanged from hydrochloric acid (1:2) after boiling the latter during one minute, the stable modification is largely transformed into β-camphornitrilic acid. It is reasonable, therefore, to represent the four monoximes of camphorquinone in the manner following:



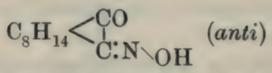
$$C_8H_{14}<\begin{array}{l}\mathrm{CO}\\ |\\ \mathrm{C{:}N}\diagup\mathrm{OH}\end{array}\ (\textit{syn})$$

α-*iso*Nitrosoepicamphor (m. p. 170°).



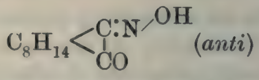
$$C_8H_{14}<\begin{array}{l}\mathrm{C{:}N}\diagdown\mathrm{OH}\\ |\\ \mathrm{CO}\end{array}\ (\textit{syn})$$

*iso*Nitrosocamphor (m. p. 152°).



$$C_8H_{14}<\begin{array}{l}\mathrm{CO}\\ |\\ \mathrm{C{:}N}\diagdown\mathrm{OH}\end{array}\ (\textit{anti})$$

β-*iso*Nitrosoepicamphor (m. p. 137°).

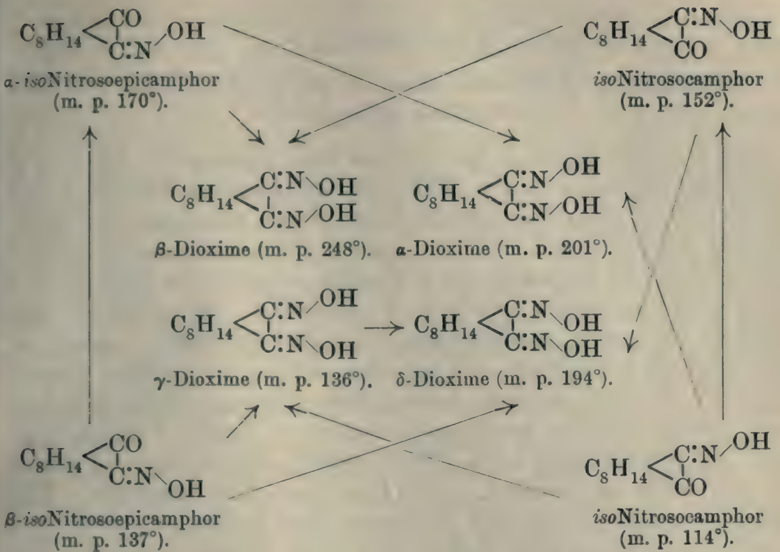


$$C_8H_{14}<\begin{array}{l}\mathrm{C{:}N}\diagup\mathrm{OH}\\ |\\ \mathrm{CO}\end{array}\ (\textit{anti})$$

*iso*Nitrosocamphor (m. p. 114°).

Passing now to the dioximes, it is at once noticeable that the γ-modification possesses in marked degree the characteristics associated with the *anti*-monoximes; it dissolves much more freely in organic media, melts at a far lower temperature, and has lower specific rotatory power than the three isomerides, into one of which (δ) it passes when heated. Being the only dioxime convertible into another, resembling in this respect the *anti*-monoximes, and displaying the attributes indicated above, it is natural to conclude that the *anti*-configuration prevails in the γ-dioxime, and as the greatest contrast is presented by the β-dioxime, it seems reasonable to regard the latter as the *syn*-modification. The two *amphi*-configurations are thus left for the α- and δ-dioximes, and in considering how these may be apportioned, cognisance must be taken of the fact that the *anti*-modification of *iso*nitrosoepicamphor is more stable than the corresponding derivative of *iso*nitrosocamphor, whence it follows that, since the change in configuration on passing from the γ-dioxime to the δ-isomeride is restricted to a single oximino-group, that group is the one present in *iso*nitrosocamphor.

The foregoing hypothesis has been submitted to a practical test by ascertaining, in the case of each dioxime, which monoximes are involved in its production. The results of this test, which are embodied in the following diagram, support the hypothesis in every particular; in fact, no one among the numerous observations which have been made in connexion with these compounds will be found in conflict with the suggestions here made as to their configuration.


$C_8H_{14}<\begin{matrix}CO\\C{:}N{\diagup}OH\end{matrix}$
α-isoNitrosoepicamphor (m. p. 170°).
$C_8H_{14}<\begin{matrix}C{:}N{\diagdown}OH\\CO\end{matrix}$
isoNitrosocamphor (m. p. 152°).
$C_8H_{14}<\begin{matrix}C{:}N{\diagdown}OH\\C{:}N{\diagup}OH\end{matrix}$
β-Dioxime (m. p. 248°).
$C_8H_{14}<\begin{matrix}C{:}N{\diagup}OH\\C{:}N{\diagup}OH\end{matrix}$
α-Dioxime (m. p. 201°).
$C_8H_{14}<\begin{matrix}C{:}N{\diagup}OH\\C{:}N{\diagdown}OH\end{matrix}$
γ-Dioxime (m. p. 136°).
$C_8H_{14}<\begin{matrix}C{:}N{\diagdown}OH\\C{:}N{\diagdown}OH\end{matrix}$
δ-Dioxime (m. p. 194°).
$C_8H_{14}<\begin{matrix}CO\\C{:}N{\diagdown}OH\end{matrix}$
β-isoNitrosoepicamphor (m. p. 137°).
$C_8H_{14}<\begin{matrix}C{:}N{\diagup}OH\\CO\end{matrix}$
isoNitrosocamphor (m. p. 114°).

Furthermore, it is worth remarking that a qualitative relationship in respect of specific rotatory power among the dioximes may be calculated in the following manner:

α-Dioxime = $\frac{1}{2}$[*iso*Nitrosocamphor (*anti*) + *iso*nitrosoepicamphor (*syn*)]
= $\frac{1}{2}$(275·3—422·0°) = −73·3°.
β-Dioxime = $\frac{1}{2}$[*iso*Nitrosocamphor (*syn*) + *iso*nitrosoepicamphor (*syn*)]
= $\frac{1}{2}$(288·0—422·0°) = −67·0°.
γ-Dioxime = $\frac{1}{2}$[*iso*Nitrosocamphor (*anti*) + *iso*nitrosoepicamphor (*anti*)]
= $\frac{1}{2}$(275·3—278·5°) = −1·6°.
δ-Dioxime = $\frac{1}{2}$[*iso*Nitrosocamphor (*syn*) + *iso*nitrosoepicamphor (*anti*)]
= $\frac{1}{2}$(288·0—278·5°) = 4·7°.

This is in qualitative agreement with the facts so far as (1) the α- and β-dioximes are both lævorotatory, (2) the α-dioxime has a higher rotatory power than the β-modification, (3) the γ-dioxime has the lowest rotatory power of all, and (4) the δ-dioxime is dextrorotatory. The above calculation is based on the values in alkali because the β-dioxime is so very sparingly soluble in organic media.

Without going into unnecessary details it may be stated that alternative relationships between the eight oximino-derivatives of camphorquinone have been considered, but these have been found, at some cardinal point or other, to be in direct conflict with experimental observation.

## EXPERIMENTAL.

### *Separation of* iso*Nitrosocamphor* (m. p. 152°) *from the Claisen Mixture.*

One hundred grams of the mixture were dissolved in 300 c.c. of ether and treated with the ferric chloride dissolved from 90 grams by 500 c.c. of ether; an intense, brownish-red coloration was immediately developed, and after an interval of twelve hours the solvent was allowed to evaporate in a current of air. On filtering the treacly residue there remained a crystalline paste, which was drained on porous earthenware, suspended in water, washed on the filter, and dissolved in 5 per cent. sodium hydroxide; a small quantity of ferric hydrate having been filtered, dilute sulphuric acid precipitated the *iso*nitroso-derivative in crystals instead of an oil. Recrystallisation from dilute methyl alcohol gave 50 grams of the stable modification quite free from the isomeride. The original mother liquor was a viscous, dark brown oil, yielding a crystalline product when shaken with water; it was hoped that this might consist of the unstable modification, but proceeding as above, an additional 30 grams of the stable isomeride was obtained. This portion was far from pure, but was suitable for the preparation of aminocamphor.

The action of ferric chloride in this process is somewhat obscure, as the amount of iron in the crystalline residue deposited from the ether is insufficient for a ferric derivative analogous to the metallic compounds obtained by Francesconi and Piazza (*Atti R. Accad. Lincei*, 1903, [v], **12**, ii, 128) from the Claisen mixture and silver nitrate or mercurous nitrate. Nevertheless, it has the effect which solvents fail to accomplish.

### *Action of Hydroxylamine on the Claisen Mixture.*

The facility with which the unstable modification of *iso*nitrosocamphor is transformed into the isomeride made it desirable to study the action of hydroxylamine in cold solutions, so that the maximum of dioxime from the former might be isolated.

Fifty grams of the Claisen mixture dissolved in 250 c.c. of alcohol and treated with a solution containing 40 grams of hydroxylamine hydrochloride and 80 grams of crystallised sodium acetate in 260 c.c. of water formed a clear liquid, from which, after twelve weeks, 40 grams of pale brown crystals had separated. On extracting this material four times with 250 c.c. of boiling acetone, 5 grams of snow-white powder consisting of almost pure $\beta$-dioxime remained. Each of the two first extracts deposited

5 grams of pure α-dioxime, the third yielding 2 grams of α-dioxime mixed with a very small proportion of β-dioxime, 0·2 gram of the latter being the only deposit from the fourth. On evaporating the acetone mother liquors, the residue weighed 19 grams, almost completely soluble in 400 c.c. of boiling acetone, which deposited 4·3 grams of α-dioxime on cooling, whilst the filtrate yielded 14 grams of brown residue when evaporated. On extracting this with cold benzene, 12·5 grams of colourless material remained, dissolving in 250 c.c. of boiling ethyl acetate, from which 4·4 grams of α-dioxime separated; reducing the mother liquor to one-half its original bulk gave 2·2 grams of α-dioxime mixed with a small proportion of δ-dioxime, still further concentration yielding 5 grams of the latter substance. Meanwhile, the mother liquor from the original 40 grams was freed from alcohol on the water-bath, when the yellow, sticky mass which separated was found to leave, on extraction with cold benzene, 7 grams of colourless dioxime, consisting principally of the δ-modification. Under the conditions stated, therefore, 50 grams of the Claisen mixture furnished approximately 23 grams of α-dioxime, 5 grams of β-dioxime, and 12 grams of δ-dioxime.

Proceeding as above with the stable modification of *iso*nitrosocamphor, and subjecting the product to systematic fractionation, the only dioximes isolated were the β- and δ-isomerides, whence it follows that the α-dioxime, which formed the major product from the Claisen mixture, must arise from the unstable *iso*nitrosocamphor present in that material.

The action of hydroxylamine in alkaline solution was then studied, 100 grams of hydroxylamine hydrochloride dissolved in water being added to an alkaline solution containing 100 grams of the Claisen mixture and 90 grams of sodium hydroxide, the total volume of water being 1000 c.c. After three weeks the liquid was extracted with ether, and fractionally acidified with dilute sulphuric acid, which precipitated a red, tarry material first, followed by a honey-like gum; as soon as the aqueous liquid failed to develop colour with ferrous sulphate, it was decanted from the precipitate, yielding 24 grams of snow-white γ-dioxime with more acid. The gummy precipitate left 6 grams of γ-dioxime when extracted with cold benzene to remove unaltered *iso*nitrosocamphor, whilst the tarry material gave 6 grams of δ-dioxime as a result of the same treatment. It having been shown already that under these conditions the stable *iso*nitrosocamphor does not yield the γ-dioxime, it follows that this substance arises from the unstable modification.

The γ-dioxime was recrystallised from methyl alcohol diluted with a small proportion of water, separating in snow-white needles melting at 136°. One per cent. solutions in chloroform, alcohol, and 2 per cent. aqueous sodium hydroxide gave $[\alpha]_D$ 16·4°, 22·7°, and 14·3° respectively.

The δ-dioxime has been obtained in condition somewhat purer than that previously described by dissolving 25 grams of the γ-dioxime in 50 c.c. of cold absolute alcohol and heating the solution under reflux during eight hours, when 13 grams of the δ-dioxime crystallised on cooling, whilst the mother liquor furnished 8 grams on concentration. Recrystallisation from methyl alcohol diluted with a small proportion of water yielded a specimen melting at 194°, giving $[\alpha]_D$ 52·8°, 80·0°, and 87·0° in chloroform, alcohol, and 2 per cent. sodium hydroxide respectively.

### *Action of Hydroxylamine on the* iso*Nitroso-derivatives of Epicamphor.*

It has been shown (T., 1912, **101**, 1353) that with hydroxylamine acetate, α-*iso*nitrosoepicamphor (m. p. 170°) yields the α- and β-dioximes, whilst the δ-dioxime is the sole product from the β-modification (m. p. 137°).

α-*iso*Nitrosoepicamphor (3 grams) dissolved in sodium hydroxide (3 grams) was treated with hydroxylamine hydrochloride (3 grams), the bright yellow solution being diluted to 30 c.c. Within a few minutes the colour had perceptibly faded, and during three days, massive, transparent crystals separated, becoming opaque when rubbed with water; this was the sodium derivative of the β-dioxime, yielding nearly 2 grams of that material. The filtrate on acidification gave 0·75 gram of β-dioxime mixed with a small proportion of the α-modification.

When β-*iso*nitrosoepicamphor was treated in the same way, the colour faded rapidly, but crystals did not separate. Fractional precipitation with dilute sulphuric acid gave (1) 1·5 gram of γ-dioxime mixed with δ-dioxime in the proportion of 2:1, and (2) 1·5 grams of almost pure γ-dioxime; thus the principal product is the γ-dioxime, with about 15 per cent. of the δ-modification.

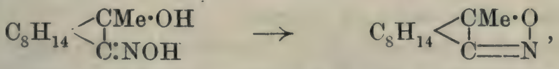
### *Action of Magnesium Methyl Iodide on* iso*Nitrosoepicamphor.*

An ethereal solution of β-*iso*nitrosoepicamphor (3 grams) was added slowly to the well-cooled Grignard agent from 1·2 gram of magnesium and 7·5 grams of methyl iodide, the product after twelve hours being decomposed with ice and acetic acid. The ethereal liquid having been extracted four times with 10 c.c. of 5 per cent. sodium hydroxide solution to remove unchanged *iso*-

nitrosoepicamphor, a crystalline residue was left on evaporation; after being recrystallised three times from dilute alcohol, the colourless needles melted at 96°:

0·1365 gave 0·3227 $CO_2$ and 0·1191 $H_2O$. C = 64·48; H = 9·76.
0·1631 ,, 10·0 c.c. $N_2$ at 22° and 758 mm. N = 6·96.
0·2836 lost 0·0128 at 100°. $H_2O$ = 4·51.
$C_{11}H_{19}O_2N$ requires C = 66·95; H = 9·71; N = 7·11 per cent.
$C_{11}H_{19}O_2N,\frac{1}{2}H_2O$ requires C = 64·02; H = 9·78; N = 6·80; $H_2O$ = 4·37 per cent.

The substance is readily soluble in organic media, including hot petroleum, but is insoluble in water. It is amphoteric, and whilst the alkaline solution remains clear when boiled, the acid solution rapidly becomes turbid when heated, doubtless owing to the transformation:



$$C_8H_{14}<\begin{matrix}CMe\cdot OH\\ \vert\\ C{:}NOH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CMe\cdot O\\ \vert\qquad\vert\\ C{=\!=}N\end{matrix},$$

just as in the case of the $\beta$- and $\gamma$-modifications of the corresponding derivative from *iso*nitrosocamphor (T., 1905, **87**, 232).

When $\alpha$-*iso*nitrosoepicamphor was treated in the same way the ethereal liquid yielded with sodium carbonate $\beta$-camphornitrilic acid, which was not produced from the isomeride; after unchanged material had been removed with sodium hydroxide the solvent deposited a viscous oil, which did not crystallise during many weeks in the desiccator. Analysis indicated a mixture of the expected oxime with its anhydride, and this fact, in conjunction with the production of $\beta$-camphornitrilic acid, may be taken as suggesting the *syn*-configuration for $\alpha$-*iso*nitrosoepicamphor.

I desire to express my indebtedness to Dr. H. Spinner for his valuable assistance in connexion with the two modifications of *iso*nitrosoepicamphor.

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South Kensington, S.W.

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# LXXV.—*Externally Compensated Hydroxyhydrazinohydrindene, its Derivatives, and Resolution into Optically Active Components.*

By David Henry Peacock.

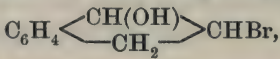
In spite of the interest attaching to the resolution of externally compensated aldehydes and ketones, very few optically active hydrazines have been prepared, and in no case has a racemic hydrazine been resolved into its optically active components. Neuberg and Federer (*Ber.*, 1905, **38**, 866) introduced the optically active amyl group into phenylhydrazine, and so obtained an active hydrazine; Kijner (*J. pr. Chem.*, 1895, [ii], **52**, 424) prepared menthonementhylhydrazine from active bromomenthylamine, and from it, by hydrolysis, the corresponding menthylhydrazine.

Bromohydroxyhydrindene has already (Pope and Read, T., 1912, **101**, 758) been converted smoothly and in quantity into the corresponding amine, hydroxyhydrindamine, which is a crystalline compound, forming easily crystallisable salts and derivatives, and is readily resolvable into its optically active components. It was therefore expected that the corresponding hydrazine compound would exhibit similar properties and be resolvable into stereoisomerides, which could then be used for the resolution of externally compensated aldehydes and ketones.

Hydroxyhydrazinohydrindene has the disadvantage of being somewhat unstable in the free state. Its salts when pure and dry are stable, but solutions of them cannot be evaporated to dryness on a water-bath without yielding a considerable quantity of a dark red solid, which melts at 182° and is insoluble in water; solutions can, however, be concentrated to a considerable extent by boiling under diminished pressure, 100 mm. and less, without very appreciable decomposition.

## EXPERIMENTAL.

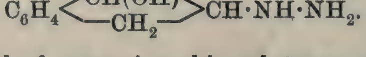
Externally compensated 2-bromo-1-hydroxyhydrindene,



$$C_6H_4{<}\begin{matrix}CH(OH)\\CH_2\end{matrix}{>}CHBr,$$

was prepared by the method of Pope and Read (T., 1912, **101**, 760), and the product, after thorough extraction with light petroleum, was dried and used without further purification.

### *Externally Compensated 1-Hydroxy-2-hydrazinohydrindene,*



$$C_6H_4{<}\begin{matrix}CH(OH)\\CH_2\end{matrix}{>}CH{\cdot}NH{\cdot}NH_2.$$

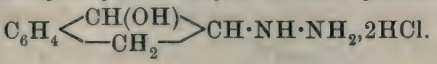
The best method of preparing this substance appears to be the following. Bromohydroxyhydrindene (50 grams) is mixed with hydrazine hydrate (50 grams) in a flask fitted with a reflux condenser, and gradually heated in an oil-bath. The mixture becomes quite liquid at 90—100°, and a reaction soon sets in so vigorously that the flask has sometimes to be cooled; when the initial vigour has abated, the flask is heated at 135—145° for two hours, and the excess of hydrazine hydrate distilled off under diminished pressure from a water-bath. The residue, when cooled, sets to a solid mass

(70 grams), which, when extracted with warm water, leaves a small quantity of insoluble residue, melting at 202—204°, and consisting of the condensation product of two molecules of bromohydroxyhydrindene with one of hydrazine. The aqueous extract is treated with solid potassium hydroxide (30 grams), and the mixture left to remain all night in a cooled exhausted vessel. The base (about 30 grams) separates as a granular solid, is filtered off through muslin, and is recrystallised from a large quantity of boiling benzene, in which it is moderately soluble. It is very sparingly soluble in cold benzene, chloroform, or ether, insoluble in light petroleum, and readily soluble in alcohol or water. It crystallises in colourless scales, melting at 87—88°, and decomposes on keeping even in an exhausted sealed tube. The following analyses were obtained with material that had been preserved two days and three days respectively:

(1) 0·188 gave 0·443 $CO_2$ and 0·124 $H_2O$. C = 64·2; H = 6·6.
(2) 0·145 „ 0·338 $CO_2$ „ 0·098 $H_2O$. C = 63·6; H = 7·5.
$C_9H_{12}ON_2$ requires C = 65·8; H = 7·3 per cent.

When carbon dioxide is passed into benzene or alcoholic solutions of the base a carbonate is precipitated.

### dl-1-*Hydroxy-2-hydrazinohydrindene Hydrochloride*,



$$C_6H_4{<}\begin{matrix}CH(OH)\\CH_2\end{matrix}{>}CH{\cdot}NH{\cdot}NH_2,2HCl.$$

This salt is precipitated on mixing alcoholic solutions of the base and hydrogen chloride, and may be prepared more directly by the following process.

Bromohydroxyhydrindene (40 grams), hydrazine hydrate (20 grams), absolute alcohol (50 grams), and pure quick-lime (20 grams) are mixed and shaken for three days in a stoppered bottle; the product is extracted with boiling absolute alcohol, filtered, cooled, and, if necessary, filtered again. Dry hydrogen chloride is then passed for some time into the cooled solution, and after remaining for two hours, the precipitated hydrochlorides are collected and extracted with a boiling mixture of benzene and alcohol, which leaves hydrazine hydrochloride undissolved; the hydrochloride of the organic base separates readily on allowing this extract to cool. The salt is readily soluble in hot absolute alcohol and water, but sparingly so in cold alcohol, boiling benzene, and ethyl acetate; it crystallises in colourless scales, melting at 165°. It contains two molecules of hydrochloric acid to one of the base, and these are retained even on recrystallisation from water. The aqueous solution does not yield a solid platinichloride with chloroplatinic acid, but gives a white precipitate with mercuric chloride; it very readily reduces copper sulphate solution:

0·1026 gave 0·1668 $CO_2$ and 0·0542 $H_2O$. C = 44·2; H = 5·7.
0·1961 „ 0·2302 AgCl. Cl = 29·1.
$C_9H_{12}ON_2,2HCl$ requires C = 45·6; H = 5·9; Cl = 29·9 per cent.

If the reaction mixture obtained by shaking as above described is extracted with boiling ethyl acetate or benzene, a crystalline precipitate is formed on cooling which crystallises from alcohol or ethyl acetate in white, shining scales, melting at 255°; this *substance* is a double compound of the hydrazine with calcium bromide:

0·1542 gave 0·1075 AgBr. Br = 29·7.
0·1351 „ 0·0928 AgBr. Br = 29·2.
$(C_9H_{12}ON_2)_2,CaBr_2$ requires Br = 30·3 per cent.

The *sulphate*, $(C_9H_{12}ON_2)_2,H_2SO_4$, is precipitated on mixing an alcoholic solution of the base with twice the calculated quantity of alcoholic sulphuric acid. It crystallises from hot dilute alcohol or water in colourless, hexagonal plates, melting and decomposing at 224°:

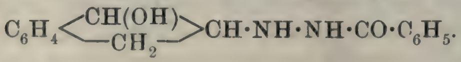
0·0987 gave 0·0531 $BaSO_4$. $SO_4$ = 22·1.
$C_{18}H_{26}O_6N_4S$ requires $SO_4$ = 22·5 per cent.

The *oxalate*, $C_9H_{12}ON_2,(CO_2H)_2$, separates on mixing alcoholic solutions of equivalent proportions of the free base and oxalic acid; after recrystallisation from hot alcohol it is obtained in colourless needles, melting at 173°. It is readily soluble in water, but sparingly so in most organic solvents, except boiling rectified spirit In both this salt and the hydrochloride the base is diacidic, whereas in the sulphate it is monacidic:

0·1660 gram gave 16·67 c.c. $N_2$ (moist) at 18° and 762 mm. N = 11·6.
$C_{11}H_{14}O_5N_2$ requires N = 11·1 per cent.

The *d*-camphor-β-sulphonate and *d*-α-bromocamphor-π-sulphonate prepared in a manner similar to the above were with difficulty obtained in a crystalline condition, owing to their hygroscopic character; they decomposed on keeping, becoming dark red.

### dl-1-*Hydroxy-2-benzoylhydrazinohydrindene*,



$$C_6H_4{<}\substack{CH(OH)\\CH_2}{>}CH\cdot NH\cdot NH\cdot CO\cdot C_6H_5.$$

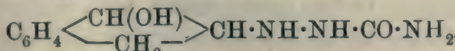
The benzoyl derivative prepared from the hydrochloride by the ordinary Schotten-Baumann process crystallises from a mixture of alcohol and acetone in small white nodules, melting at 196°. Benzoylation in pyridine solution with two molecules of benzoyl chloride yielded only the monobenzoyl derivative:

0·1184 gave 0·3010 $CO_2$ and 0·0620 $H_2O$. C = 69·4; H = 5·9.

$C_{16}H_{16}O_2N_2$ requires C = 71·6; H = 5·9 per cent.

The hydrochloride when heated with acetic anhydride yielded an oil which could not be caused to crystallise; bromohydroxyhydrindene behaves in the same way. The benzenesulphonyl- and *p*-toluenesulphonyl derivatives could not be prepared by the ordinary Schotten-Baumann process, black, uncrystallisable resins being produced.

### dl-1-*Hydroxy-2-semicarbazinohydrindene*,



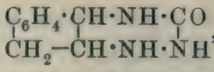
$$C_6H_4\left\langle\begin{matrix}CH(OH)\\-CH_2-\end{matrix}\right\rangle CH\cdot NH\cdot NH\cdot CO\cdot NH_2.$$

This compound is obtained in quantitative yield when aqueous solutions of equimolecular proportions of the hydrochloride of the base and potassium cyanate are mixed and left to remain for an hour; it separates as a white, amorphous powder, which crystallises from hot spirit in minute scales, melting at 195°. It dissolves sparingly in most organic solvents, in water or dilute acid, and is moderately soluble in hot alcohol, benzene, or concentrated hydrochloric acid; it is very stable, and its solutions can be evaporated to dryness without decomposition:

0·1255 gave 21·4 c.c. $N_2$ (moist) at 20° and 758 mm. N = 19·4.

$C_9H_{13}O_2N_3$ requires N = 20·1 per cent.

On dissolving the semicarbazide in concentrated sulphuric acid some blackening occurs, but, if the solution is left for two hours and then poured into water and filtered, a yellow solution with a green fluorescence is obtained. This may contain the compound:

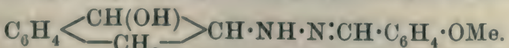


$$\begin{matrix}C_6H_4\cdot CH\cdot NH\cdot CO\\ CH_2-CH\cdot NH\cdot NH\end{matrix},$$

and, if so, the hydroxy- and hydrazino-groups in the parent substance are probably in the *cis*-position.

On attempting to prepare the thiosemicarbazide by a similar method no solid separated, and on evaporating the solution the main product was the thiocyanate, which crystallises in colourless rosettes, melting at 112°, and turning pink on keeping.

### dl-1-*Hydroxy-2-anisylidenehydrazinohydrindene*,



$$C_6H_4\left\langle\begin{matrix}CH(OH)\\-CH_2-\end{matrix}\right\rangle CH\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OMe.$$

The hydrochloride of the base is dissolved in a solution containing rather more than two molecular equivalents of sodium acetate and a little acetic acid. The calculated weight of anisaldehyde is then added to the hot solution, which is well shaken and heated in a boiling-water bath for two hours. On cooling, the hydrazone separates as a solid mass, which is collected, washed with ether, and recrystallised first from hot alcohol, and then from hot benzene, from which it separates in small, flat, yellow scales, melting at 168°:

0·1436 gave 12·6 c.c. $N_2$ (moist) at 17° and 744 mm. N = 9·97.
$C_{17}H_{18}O_2N_2$ requires N = 9·92 per cent.

dl-1-*Hydroxy-2-cinnamylidenehydrazinohydrindene* was prepared in a similar way, but this compound separated in the cold as an orange-yellow solid, which seemed somewhat unstable, and was difficult to purify. It was precipitated as a yellow powder from its alcoholic solution by light petroleum, and melted at 124°:

0·1175 gave 0·3328 $CO_2$ and 0·0575 $H_2O$. C = 77·3; H = 5·5.
$C_{18}H_{18}ON_2$ requires C = 77·7; H = 6·4 per cent.

dl-1-*Hydroxy-2-benzylidenehydrazinohydrindene* was prepared similarly to the anisic compound; it crystallises from hot rectified spirit in small, white needles, melting at 107°.

The *vanillylidene* compound, prepared as above, was very difficult to purify; it was recrystallised from a hot mixture of methyl alcohol and benzene, and separated in small, yellow scales, melting at 161°:

0·1316 gave 10·67 c.c. $N_2$ (moist) at 16° and 746 mm. N = 9·28.
$C_{17}H_{18}O_3N_2$ requires N = 9·39 per cent.

The *salicylidene* compound prepared similarly crystallised from hot spirit in shining, yellow scales, melting at 213°.

The *piperonylidene* compound was, like that of vanillin, very difficult to purify; it was recrystallised several times, and finally separated from benzene in yellow scales, melting at 201°:

0·1053 gave 8·6 c.c. $N_2$ (moist) at 17° and 755 mm. N = 9·58.
$C_{17}H_{16}O_3N_2$ requires N = 9·46 per cent.

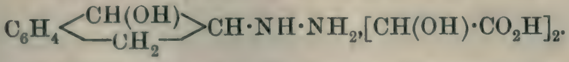
The *nitropiperonylidene* compound was easily prepared in a very good yield by the usual method. It was recrystallised twice from hot rectified spirit, and obtained in orange-red needles, melting at 142°:

0·1590 gave 16·67 c.c. $N_2$ (moist) at 20° and 758 mm. N = 11·9.
$C_{17}H_{15}O_5N_3$ requires N = 12·3 per cent.

The *benzoylmethylene* compound prepared in the usual manner was obtained in a very poor yield; after precipitation by light petroleum from its solution in rectified spirit, it melted at 96°.

Neither dextrose nor lævulose precipitated hydrazones on being treated in the above manner, nor when left in contact with an alcoholic solution of the free base. An attempt to prepare an osazone by the usual method only yielded tarry decomposition products.

### 1-*Hydroxy-2-hydrazinohydrindene* d-*Tartrate*,



$$C_6H_4<\begin{matrix}CH(OH)\\CH_2\end{matrix}>CH\cdot NH\cdot NH_2,[CH(OH)\cdot CO_2H]_2.$$

On mixing an alcoholic solution of the externally compensated hydrazine, which had been recrystallised from benzene, with an alcoholic solution of the equimolecular proportion of *d*-tartaric acid, the *d*-tartrates were precipitated, being almost insoluble in rectified spirit. After five recrystallisations from boiling aqueous alcohol, the mixture was found to be resolved, the less soluble component being the salt *lBdA*, containing the *l*-base. This salt is sparingly soluble in cold water, very sparingly soluble in cold alcohol, and readily soluble in hot water and boiling dilute alcohol, from which latter solvent it separates in very fine colourless needles, melting at 195—196°:

0·1002 gave 0·1856 $CO_2$ and 0·0624 $H_2O$. C=50·5; H=6·6.

$C_{13}H_{18}O_9N_2$ requires C=49·6; H=5·7 per cent.

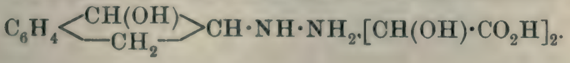
| | 0·2406 gram in water. | | | 0·2854 gram in water. | |
|---|---|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. | $Hg_{green}$. | $Hg_{yellow}$. |
| α ........ | -0·125° | -0·085° | 0° | -0·15° | -0·10° |
| [α]........ | 3·90 | 2·66 | 0 | 3·94 | 2·62 |
| [M] ...... | 12·2 | 8·34 | 0 | 12·4 | 8·2 |

Mean values, [M]: $Hg_{green}$ -12·3°; $Hg_{yellow}$ -8·27°.

Rotatory dispersion: $Hg_{green}/Hg_{yellow}$=1·48. No mutarotation was observed.

The solutions were made up to 30 c.c., and measured in 4-dcm. tubes at 20°, except where otherwise stated.

### d-1-*Hydroxy-2-hydrazinohydrindene* d-*Tartrate*,



$$C_6H_4<\begin{matrix}CH(OH)\\CH_2\end{matrix}>CH\cdot NH\cdot NH_2.[CH(OH)\cdot CO_2H]_2.$$

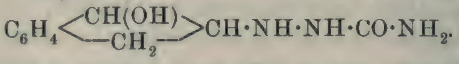
This salt was not obtained in a pure state. On leaving the solutions, from which the more sparingly soluble salt had been separated, to remain, a further crop of crystals was obtained; the less soluble portion was removed from this by fractional recrystallisation, and finally a salt was obtained, melting at 168—169°, this being unchanged by further recrystallisation. The following rotations were observed with two specimens prepared in this way:

| | 0·177 gram in water. | 0·320 gram in water. | |
|---|---|---|---|
| | $Hg_{green}$. | $Hg_{green}$. | $Hg_{yellow}$. |
| α .............. | +0·60° | +1·16° | +1·05° |
| [α].......... ..... | 25·4 | 27·2 | 24·6 |
| [M] ..... ...... | 79·8 | 85·4 | 75·9 |

0·1791 gave 0·3200 $CO_2$ and 0·0945 $H_2O$. C = 48·7; H = 5·8.
$C_{13}H_{18}O_9N_2$ requires C = 49·6; H = 5·7 per cent.

The resolution by means of tartaric acid could not be effected by the equilibrium method. On dissolving one molecular proportion of the tartrate and of the hydrochloride in hot water or hot dilute alcohol and allowing the solution to cool, the first crystals that separated contained both salts, *lBdA* and *dBdA*, and the hydrochloride recovered from the solution showed only a very slight activity.

### l-1-*Hydroxy-2-semicarbazinohydrindene*,



$$C_6H_4{<}\begin{matrix}CH(OH)\\CH_2\end{matrix}{>}CH\cdot NH\cdot NH\cdot CO\cdot NH_2.$$

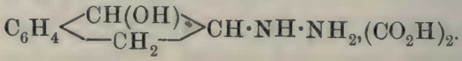
The compound separated on mixing warm aqueous solutions of the active tartrate and potassium cyanate; it was recrystallised from rectified spirit, and obtained in shining scales, melting at 196°:

0·1202 gave 0·2515 $CO_2$ and 0·0633 $H_2O$. C = 57·1; H = 5·8.
$C_{10}H_{13}O_2N_3$ requires C = 58·2; H = 5·8 per cent.

0·1530 gram, in rectified spirit, gave for $Hg_{green}$ light, $\alpha - 0·30°$; whence $[\alpha] - 14·7°$ and $[M] - 28·6°$.

No mutarotation was observed.

### l-1-*Hydroxy-2-hydrazinohydrindene Oxalate*,



$$C_6H_4{<}\begin{matrix}CH(OH)\\CH_2\end{matrix}{>}CH\cdot NH\cdot NH_2,(CO_2H)_2.$$

The tartrate of the *l*-base was mixed in hot water with the calculated quantity of crystalline barium hydroxide; the precipitated barium tartrate was removed by filtration, the calculated quantity of oxalic acid added, and the solution left to cool. The oxalate then separated in colourless rosettes, melting at 178°; it crystallises from dilute alcohol in needles:

0·1095 gave 0·2055 $CO_2$ and 0·0563 $H_2O$. C = 51·2; H = 5·66.
$C_{11}H_{14}O_5N_2$ requires C = 51·9; H = 5·5 per cent.

| | 0·1126 gram in water. | | |
|---|---|---|---|
| | $Hg_{green}$. | $Hg_{yellow}$. | $Na_{yellow}$. |
| $\alpha$ | − 0·33° | − 0·265° | − 0·21° |
| $[\alpha]$ | 21·98 | 17·65 | 13·98 |
| $[M]$ | 55·82 | 44·82 | 35·53 |

Rotatory dispersions: 1·24; 1·26.

The rotatory dispersion $Hg_{yellow}/Na_{yellow}$ is remarkably high; no mutarotation was observed.

The tartrates of the active bases could not be used for the direct preparation of hydrazones, as on heating a solution of the tartrate in presence of sodium acetate and acetic acid with either nitropiperonaldehyde or anisaldehyde a tarry mass resulted; a similar result was obtained in alcoholic solution. The oxalates would seem to be more suitable for the preparation of the hydrazones.

In conclusion I wish to thank Prof. Pope for suggesting this work, and for the interest he has taken in it.

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# LXXVI.—*The Action of Ozone on Cellulose. Part III. Action on Beech Wood (Lignocellulose).*

By CHARLES DORÉE and MARY CUNNINGHAM.

IN a former paper (T., 1912, **101**, 503) an account has been given of some experiments relating to the nature of the action of ozone on normal cotton cellulose and the lignocellulose jute.

Of the lignocellulose group, jute represents an elementary type, being an annual growth of comparatively simple structure and composition. In the woods, on the other hand, which are perennial, the changes embodied in the term lignification are of necessity more advanced, and their tissue, although in many respects similar to that of jute, is more complex, both in structure and composition. The results obtained, however, showed that ozone was likely to prove a very suitable reagent for the investigation of such complex natural substances. It has the merit of extreme simplicity—the oxidising system, from a stoicheiometrical point of view, consisting only of oxygen and water, and the reagent, being employed as a diluted gas, is always under perfect control, both as to its concentration and the duration of its action.

In the present communication, therefore, we have extended these observations to the lignocellulose of the woods, beech wood being chosen as a fairly well investigated type. The results obtained have been compared and examined critically in their relation to jute, and finally are discussed in their bearing on the difficult question of the constitution of the lignone complex.

## EXPERIMENTAL.

The very thin beech shavings were steeped in water and treated several times with alcohol in the cold. All weighings were made on air-dry material, the dry weights given being calculated from the loss in weight of a duplicate sample. Determinations of moisture were made by drying in the water-oven. Water free from air was used throughout.

The ozonised oxygen used had a concentration of about 1·5 grams per 100 grams, or one part (c.c.) per 100 parts (c.c.). Purified and dried oxygen was used, and passed at a rate of 5 to 8 litres per hour through an ozoniser of the Andreoli type. The ozone was found to be absolutely free from oxides of nitrogen.

The constants of the wood substance were determined in the usual way, the copper numbers being estimated by Schwalbe's method ("Chemie der Cellulose," 1911, p. 625). The general method of experiment was the same as that previously described. The shavings were sprayed with water, and packed loosely in tall towers, through which the ozonised oxygen was continuously passed. The carbon dioxide produced in the oxidation was estimated by absorption in barium hydroxide solution and titration with $N/20$-acid (the results are given as $N/10$-acid). The "acidity" of the residual wood was measured by washing the contents of the tower into a beaker and titrating with $N/10$-sodium hydroxide solution until neutral to phenolphthalein. After remaining covered for one hour, additional alkali was added until the pink colour returned, and the total quantity used taken as a measure of the acidity developed. Unlike jute, the wood was not bleached by extended treatment with ozone in the presence of water. It was very rapidly attacked, however, absorbing the ozone completely, and after a time became thin and friable. It had a nauseous odour, due to the presence of acids partly volatile in steam.

### *The Progressive Action of Ozone on Beech Wood in the Presence of Water.*

Quantities of about 2 grams were ozonised for varying periods under comparable conditions. With such quantities, the ozone was always in excess. After titration with $N/10$-sodium hydroxide solution, the residue was collected, washed with dilute acetic acid and water, dried, and weighed. The results are given in table I, the values previously found for jute being given in brackets. All the figures are calculated on 100 grams of dry substance.

These numbers are very similar to those found for jute. The loss in weight of the beech in the first three hours is exactly the same, namely, 7 per cent. per hour. In the next three hours the rate of loss has fallen to three, and in the last six hours to 1·3 per cent. per hour, compared with 0·7 and 1 per cent. respectively for

TABLE I.

*Progressive Action of Ozone on Beech Wood.*

| Time in hours. | *N*/10-NaOH. c.c. | $CO_2$ as *N*/10 acid. c.c. | Ratio $\frac{NaOH}{CO_2}$. | $CO_2$ weight per cent. | Fibre loss in weight. |
|---|---|---|---|---|---|
| 1 | 525 | 291 | 1·8 | 0·65 | 7·5 |
| | *(493)* | *(146)* | | | *(7·5)* |
| 3 | 1926 | 998 | 1·9 | 2·20 | 21·6 |
| | *(1406)* | *(1123)* | | | *(21·7)* |
| 6 | 3018 | 1881 | 1·6 | 4·15 | 31·0 |
| | *(2000)* | *(2300)* | | | *(24·0)* |
| 12 | 3320 | 3140 | 1·1 | 6·90 | 38·9 |
| | *(2700)* | *(3000)* | | | *(30·0)* |

jute. The lignone reactions were obtainable throughout, but they were weak after twelve hours, and still more so after twenty-four hours (compare T., 1912, **101**, 507).

The acidity developed in the substance is produced rapidly and regularly for the first six hours, the amount being roughly 500 c.c. per cent. per hour. In the next six hours, however, the rate has fallen to 50 c.c. per hour. In the case of jute the initial rate is the same, but the marked fall in the rate of production occurs after three hours instead of after six. The carbon dioxide produced is at first very much less than this acidity. For the first six hours it also is uniform and roughly about 300 c.c. per hour. In the final six hours, however, it is still being formed at the rate of 200 c.c. per hour. There is thus an initial rapid production of acidic compounds in the wood substance, which after six hours falls to one-tenth of its value, accompanied by an initially less rapid, but almost uniform production of carbon dioxide, the acidity and the carbon dioxide becoming equal after twelve hours. These results would seem to show that the first effect of the ozone is to attack the less resistant lignone groupings, as was established in the case of jute (*loc. cit.*, p. 506), converting them into acid derivatives. This process continues until about 30 per cent. of the wood substance is found to be removed after neutralisation with *N*/10-alkali. The ozone then attacks the residual cellulose fibre more slowly, the loss of weight being only 9 per cent. in the final six hours, but continues to oxidise the acid substances first formed, so that the production of carbon dioxide continues uniformly. In order to ascertain what changes had taken place in the wood substance, the following experiments were carried out.

### *The Nature of the Products obtained after more Prolonged Treatment with Ozone.*

*Experiment A.*—Twenty grams of fine shavings sprayed with water were submitted to a rapid current of ozone for twenty-four hours. The whole of the ozone was absorbed by the beech, and to secure uniformity of action the towers were frequently reversed and the contents mixed. The exposure may be regarded perhaps as equivalent to one of fifteen hours only. The shavings became red in places and bleached slightly at the edges, but very little colour change was apparent on drying. The contents of the towers were steeped in water, giving a turbid liquid, which was distilled in a current of steam until acids ceased to distil over.

(i) The distillate measured 5·5 litres, and contained minute floating particles (compare cotton and jute). It required 77 c.c. of *N*/10-sodium hydroxide for neutralisation, or 385 c.c. per hundred grams of beech, equivalent to 2·26 per cent. calculated as acetic acid. Qualitative tests indicated the presence of acetic and formic acids as silver nitrate and mercuric chloride were reduced, but as reduction also occurred with ammoniacal silver nitrate some other reducing acid was no doubt present. The distillate also showed a slight reducing power towards Fehling's solution, and gave no reactions indicative of phenols. It gave an amorphous precipitate on warming with phenylhydrazine acetate, which could not be characterised, but on one occasion after treatment with phenylhydrazine needle-shaped crystals separated, which were picked out and found to melt at about 105°, agreeing with the melting point of lævulic acid phenylhydrazone. The quantity was too small for investigation, and the preparation could not be repeated.

(ii) The water digest after filtering from the residual wood was deep yellow and strongly acid, producing smarting on the skin. It turned red on being rendered alkaline. Its volume was 820 c.c., and it required 238 c.c. of *N*/10-sodium hydroxide to neutralise it, or 1190 c.c. per cent. It gave a trace of precipitate with lime-water insoluble in acetic, but soluble in hydrochloric acid, pointing to the presence of a little oxalic acid, and a yellow precipitate with lead acetate soluble in excess. It strongly reduced Fehling's solution, and both neutral and ammoniacal silver nitrate solutions on warming, and also potassium permanganate.

(iii) The residual wood (product *A*) contained 10·7 per cent. of moisture, and weighed 16·78 grams, equivalent to 14·97 grams of dry material. Loss in weight, 25 per cent. The constants are given below.

*Experiment B.*—11·52 Grams were ozonised in a very rapid stream of gas for thirty-six hours with the same precautions to secure even action, as in experiment A. At the end ozone was passing in excess. The contents of the bottle were digested with $1\frac{1}{2}$ litres of water at 90° for some hours, filtered, and washed. The residual wood (product *B*) was dried at 98°, and weighed 6·82 grams or 59·2 per cent. Loss in weight, 40·8 per cent. The filtrate was distilled to small bulk to remove as far as possible the volatile acids, and one-half of the liquid remaining in the flask was evaporated to dryness and furfuraldehyde was estimated in it.

One-half gave 0·1520 gram of furfuraldehydephloroglucide. Total furfuraldehyde found = 0·1630 gram. This represents 1·42 per cent., calculated on the original wood taken, or 3·4 per cent. on the soluble portion, assuming that this is represented by the difference between the original weight taken and that of the residue left after the ozone and water treatment.

The other half was also evaporated, and a methoxyl estimation gave AgI = 0·068. Total methoxyl found = 0·16 per cent. on the original weight of beech, or 0·4 per cent. on the soluble portion.

## *Properties of the Residual Wood.*

(i) *The Beech Wood.*—The "constants" of the beech wood used for experiment were determined as follows:

Hygroscopic moisture = 8·2.

Loss on boiling in 1 per cent. NaOH for five minutes = 12·2.

0·9832 gave 0·2801 furfuraldehyde-phloroglucide. Furfuraldehyde = 15·02.

1·876 gave 0·0606 copper. Copper reduced = 3·23.

0·2902 „ 0·1368 AgI. $OCH_3$ = 6·2 per cent.

(ii) Product *A*.

Hygroscopic moisture = 10·8.

Loss on boiling in 1 per cent. NaOH = 18·75.

0·0915 gave 0·1631 $CO_2$ and 0·0518 $H_2O$. C = 48·61; H = 6·29.

1·714 „ 0·2372 furfuraldehyde-phloroglucide. Furfuraldehyde = 14·68.

(iii) Product *B*.

Loss in 1 per cent. NaOH = 30·63 per cent.

0·1282 gave 0·2736 $CO_2$ and 0·0679 $H_2O$. C = 46·84; H = 5·87.

1·056 „ 0·2751 furfuraldehyde-phloroglucide. Furfuraldehyde = 13·75.

1·2035 gave 0·1633 copper. Copper reduced = 13·57 per cent.

These results are collected in the following table, the values previously obtained for jute (*loc. cit.*, p. 509) being included:

TABLE II.

| | Original beech. | Product *A*. Ozone, 15 hours. | Product *B*. Ozone, 30 hours. | Original jute. | Jute. Ozone, 6 hours |
|---|---|---|---|---|---|
| Residue | 100·0 | 74·9 | 59·2 | 100·0 | 67·3 |
| Loss in weight | — | 25·1 | 40·8 | — | 32·7 |
| Composition C | 49·1 | 48·61 | 46·84 | 46·5 | 43·81 |
| ,, H | 5·6 | 6·29 | 5·87 | 6·0 | 6·41 |
| O, H ratio | — | 7·1 | 8·1 | 8·0 | 7·8 |
| Furfuraldehyde* | 15·0 | 14·68 | 13·75 | 7·8 | 5·77 |
| Furfuraldehyde: † | | | | | |
| (*a*) in fibre | — | 11·02 | 8·14 | — | 3·95 |
| (*b*) in solution | — | — | 1·42 | — | 1·45 |
| Total furfuraldehyde | 15·0 | — | 9·56 | 7·8 | 5·4 |
| Methoxyl* | 6·22 | — | 3·2 | — | — |
| Copper number | 3·23 | — | 13·57 | — | — |
| Loss 1% NaOH (5 mins.) | 12·20 | 18·75 | 30·63 | 9·4 | 16·0 |

* Calculated as yielded by 100 grams of the product.

† Calculated as yielded by 100 grams of original material.

It will be seen that oxidation by ozone in the presence of water for thirty hours and subsequent digestion with water removes 40 per cent. of the wood substance. Part of this is oxidised to carbon dioxide and acetic and formic acids; another part is made soluble in water, and passes into solution in a more or less modified form. The water-soluble part still yields 1·42 per cent. of furfuraldehyde (on 100 grams of beech taken) out of the 15 per cent. given by the original wood. The solid residue yields 8·14 per cent., so that, assuming no development of furfuraldehyde-yielding groups to occur during the oxidation, there is a reduction of the total furfuraldehyde yield from 15 to 9·56, or 5·44 per cent. This may point to a destruction of 36 per cent. of the furfuraldehyde-yielding complex, so that the "balance sheet" of this constituent may be as follows:

| | Beech. | Jute. |
|---|---|---|
| Remaining in the woody product | 54 | 50 |
| Remaining in the soluble portion | 10 | 19 |
| "Destroyed" | 36 | 31 |
| | 100 | 100 |

The jute fibre can be regarded as a complex of:

| α-Cellulose. | β-Cellulose. | Lignone. |
|---|---|---|
| 65 | 15 | 20 |

(Cross and Bevan, "Researches," I., 135.)

Of these the β-cellulose yields practically the whole of the furfuraldehyde, some 8 per cent. The fact that treatment with ozone until the lignone reaction disappears results in a loss of 33 per cent. in weight would be accounted for by the assumption that the whole of the lignone and half the β-cellulose were removed. This would require a loss of 28 per cent., and other experiments showed (T., 1912, **101**, 506) that the α- and β-cellulose are also slightly attacked, making up the additional loss of about 5 per cent.

The beech wood used in these experiments was not boiled with alkali, but only extracted with water and alcohol. It might therefore contain some 5—10 per cent. of "wood gum," a substance giving 30 to 50 per cent. of furfuraldehyde, so that the statistical calculation in this case is not so satisfactory as with jute. The time experiments have shown, however, that ozone attacks the lignified portions of the beech rapidly at first, but later the attack is confined chiefly to the already oxidised lignone, and also partly to the cellulose portion; thus, during the last six hours some of the β-cellulose is either oxidised completely to carbon dioxide or converted to soluble products. With the thirty-hour product *B*, the loss of weight of 40 per cent. is therefore also probably due to the removal of nearly all the lignone, together with some proportion of the β-cellulose. In this respect the action is similar to that taking place in the bisulphite process, in which the lignone is removed largely in combination with the β-cellulose, the loss being some 50 per cent., and differs from the action of chlorine, in which the lignone alone is removed, the loss of weight then amounting to 40 per cent. in the case of beech wood. This would account for the reduction of the furfuraldehyde content from 15 to 8 per cent., and also for the fact that the product *B* does not, as with jute, show the composition of an oxycellulose. The jute fibre lost 33 per cent. of its weight, and gave a product containing 43·8 per cent. of carbon, and yielding 5·7 per cent. of furfuraldehyde, agreeing in composition and properties with an oxycellulose of high furfuraldehyde content. That this was the α- and β-cellulose of the jute was shown by the observation that on chlorination no lignone reactions were observed, and practically no further loss of weight took place (*loc. cit.*, p. 507). In the case of beech, however, with a loss of weight of 40 per cent. the product still contains 46·6 per cent. of carbon, and yields 13·7 per cent. of furfuraldehyde. It has an oxygen hydrogen ratio of 8:1, and in composition is thus very similar to jute itself. It has acquired oxycellulose characters, notably a copper number of 13·6 compared with 3·2, and its solubility in dilute sodium hydroxide has become 30·6 instead of 12·2 per cent.

The methoxyl content of product *B* is also very significant. The values obtained were confirmed by duplicate experiments, and show that whereas the beech yielded 6·2 per cent. of methoxyl, product *B* only yielded 3·2 per cent., or 1·92 per cent., calculated on the original weight of the beech. At the same time, only 0·16 per cent. was found in the soluble portion, so that the percentage distribution of this constituent would be: in the solid portion, 31; in solution, 2·6; destroyed, 66·4 per cent. These figures indicate an oxidation of 66 per cent. of the groups containing methoxyl. These are known to be situated largely in the lignone complex, but also to a lesser extent in the β-cellulose portion of the lignocellulose. Cross and Bevan, for example, found (*Ber.*, 1893, **26**, 2520) that with an original jute containing 4·5 per cent. of methoxyl the α- and β-cellulose isolated from it contained 1·2 per cent. These values indicate that 84 per cent. of the methoxyl groupings are present in the lignone and 16 per cent. in the cellulose. In beech product *B* 31 per cent. is present.

These results all point to the conclusion that product *B*, the residue from a prolonged treatment with ozone, consists of the α-cellulose, part of the β-cellulose, and (unlike the jute product) of a proportion of some lignified constituent. The latter can be accounted for by the fact that apart from the "wood gum," the lignified portions of the woods of long growth are more complex than those of the annual fibre jute.

The product *A*, fifteen hours treatment, shows intermediate characters, the loss of weight being 25 per cent. and the furfuraldehyde in the solid substance being 11 instead of 15 per cent. Its composition (C = 48·6; H = 6·3) differs only slightly from that of the original beech, and indicates the gradual oxidation of the lignone portion.

### *The Nature of the Action of Ozone on Lignocellulose.*

The experimental work on jute and beech has resulted in the following observations of which an explanation must be sought.

(1) Ozone has practically no action on the dry substance. In anhydrous media the action is one of slow oxidation.

(2) In the presence of water there is a rapid initial development of acid products, followed by a fall in the production to one-tenth of the former value in the case of beech.

(3) Carbon dioxide is produced throughout, the decrease in the rate of production after six hours being small.

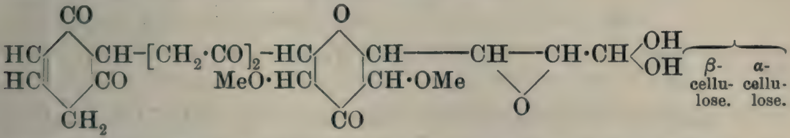
(4) Volatile acids, namely, 2·6 per cent. (beech) and 2·5, 5·5, and 3·5 per cent. (jute), calculated as acetic acid, are obtained on distillation in steam. These consist of acetic and formic and another acid of reducing character (beech). With jute the proportion of formic acid is 30—50 per cent. of the total volatile acid.

(5) The non-volatile acid liquid has three to five times the acid value of the volatile acids. It contains reducing substances of an aldehydic or ketonic character. Oxalic acid is present only in minute quantity; phenols are absent.

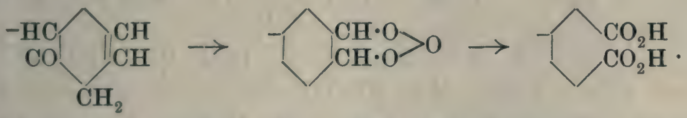
(6) Some 40 per cent. of the wood is oxidised or rendered soluble in water.

(7) The solid product has a high furfuraldehyde content, but contains only a small proportion of methoxyl.

The schematic formula which embodies the known reactions of lignocellulose given by Cross and Bevan ("Researches," III., p. 104) formulates the lignone group as (*a*) a keto-R-hexene group joined by $CH_2 \cdot CO$ residues to (*b*) a pyrone ring containing two methoxyl groups, this ring being connected through a chain of carbon atoms to the β- and α-cellulose, thus:



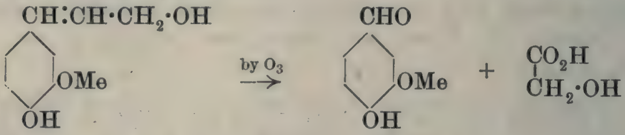
The ozone molecule attaches itself, in the absence of water, to unsaturated linkings forming ozonides; in the presence of water these ozonides are decomposed at the moment of formation, yielding aldehydes or acids. With the *cyclo*hexenone group (*a*) the result would probably be:



This would account for the rapid initial development of acidic substances, the ozone being entirely absorbed at the unsaturated linking. At the same time, the opening up of the ring at this point determines (as with chlorine) the removal of the whole of the lignone from the cellulose complex. In this case the β-cellulose is partly removed, also in combination with the lignone, as in the bisulphite process. Further oxidation of these groupings at once begins. The formation of acetic acid indicates the rupture of the attachment between the *cyclo*hexenone and the pyrone groups. The former group probably gives acids of a ketonic character accounting for the powerful reducing properties of the water digest. The pyrone grouping in its oxygen atom and carbonyl group presents to ozone two points of attack. Unstable peroxides will probably be formed, the decomposition of which will further the process of oxidation. The fact that only 30 per cent. of the methoxyl constituent is found in the wood residue points to the almost complete destruction of this grouping, and by the cleavage of such a pyrone ring formic acid could easily be produced.

The results, so far as they carry, therefore, are fully in agreement with the formulation of the lignocellulose complex proposed by Cross and Bevan. On the other hand, they do not lend support to the alternative view of Klason (*Beiträge zur Kentniss der chemischen Zusammensetzung des Fichtenholzes*, Berlin, 1911), that the "lignin" (of coniferous woods) is largely of an aromatic nature, being based on coniferyl alcohol (I) and of a condensed anhydride of hydroxyconiferyl alcohol or allied compound.

If this were the case, the action of ozone should yield vanillin (II) in considerable quantity, thus:



(I.) (II.)

In none of the products obtained, however, could this aldehyde be detected. It might be urged that if formed it would be at once oxidised by ozone to simpler derivatives. Aldehydes, however, are remarkably stable towards ozone, and vanillin is at the present time largely manufactured by the oxidation of *iso*eugenol by ozone, according to the observation first made by Otto (*Ann. Chim. Phys.*, 1898, [vii], **13**, 77). It is true that vanillin has been obtained from woods by various processes of hydrolysis and oxidation (Singer, *Monatsh.*, 1882, **3**, 409; Grafe, *ibid.*, 1904, **25**, 1004; Czapek, *Zeitsch. physiol. Chem.*, 1899, **27**, 141), but only in minute quantity (40 grams from 50 kilos. by Czapek and Grafe). The quantity, if any, produced by ozone must be of a similar order, and this seems to preclude the possibility of any considerable portion of the lignone complex having the coniferyl alcohol basis. Klason further states that the lignin (of coniferous woods) does not yield any acetic acid on oxidation. There is no reason to suppose that the lignin of pinewood differs essentially from that of beech and jute, yet with both of these a considerable production of acetic acid can be observed as the result of an hour's exposure to dilute ozone. This must surely proceed from the oxidation of the reactive lignone groupings.

Experiments are now in progress which will, it is hoped, throw further light on these problems.

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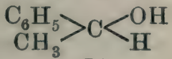
# LXXVII.—*Experiments on the Walden Inversion.* Part IX. The Interconversion of the Optically Active Phenylmethylcarbinols.*

By Alex. McKenzie and George William Clough.

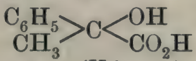
Previous researches on the Walden inversion have been confined to transformations undergone by carboxylic acids or by their more closely allied derivatives, such as esters. Although the picture of the Walden inversion may not now be very materially altered by an extension of the experimental inquiry to other types, it is nevertheless desirable that such an extension should be prosecuted in order to provide further data for the discussion of the problem on the theoretical side. On this account a study has been made of the phenylmethylcarbinols, and the enantiomorphously related isomerides have been converted one into the other.

Thanks to the work of Pickard, Kenyon, and others, it is now possible to obtain a whole series of optically active alcohols by the resolution of the *dl*-forms. The phenylmethylcarbinols (I) were



$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\H\end{matrix}$

(I.)

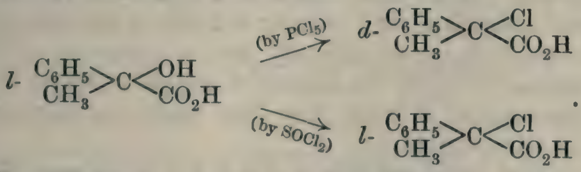


$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix}$

(II.)

selected for the present purpose in order to contrast their behaviour with that of the α-hydroxy-α-phenylpropionic acids (II), which had already been studied. Moreover, the presence of a phenyl group in other compounds causes group displacement to be accompanied by racemisation to a degree which is generally considerable. It was therefore of some interest to find out if a similar effect would be observed in the case of the phenylmethylcarbinols.

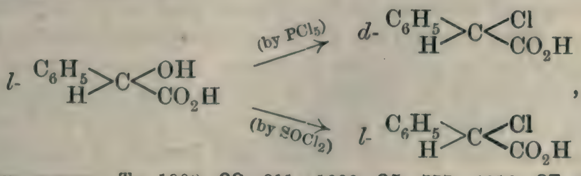
Phosphorus pentachloride and thionyl chloride behave differently towards *l*-α-hydroxy-α-phenylpropionic acid, thus:



$$l\text{-}\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix}\ \xrightarrow{\text{(by }PCl_5)}\ d\text{-}\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}Cl\\CO_2H\end{matrix}$$

$$l\text{-}\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix}\ \xrightarrow{\text{(by }SOCl_2)}\ l\text{-}\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}Cl\\CO_2H\end{matrix}.$$

A similar difference in behaviour was observed in other instances, thus, with *l*-mandelic acid:



$$l\text{-}\begin{matrix}C_6H_5\\H\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix}\ \xrightarrow{\text{(by }PCl_5)}\ d\text{-}\begin{matrix}C_6H_5\\H\end{matrix}\!>\!C\!<\!\begin{matrix}Cl\\CO_2H\end{matrix}$$

$$l\text{-}\begin{matrix}C_6H_5\\H\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix}\ \xrightarrow{\text{(by }SOCl_2)}\ l\text{-}\begin{matrix}C_6H_5\\H\end{matrix}\!>\!C\!<\!\begin{matrix}Cl\\CO_2H\end{matrix},$$

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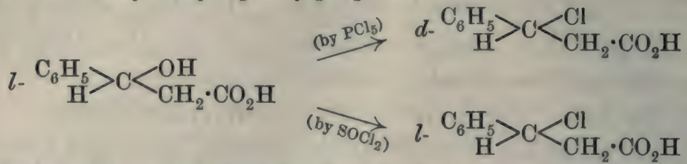
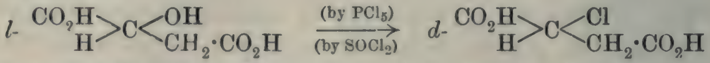
* Previous papers: T., 1908, **93**, 811; 1909, **95**, 777; 1910, **97**, 121, 1016, 1355, 2564; 1911, **99**, 1910; 1912, **101**, 390.

and with *l*-β-hydroxy-β-phenylpropionic acid:



$$l\text{-}\genfrac{}{}{0pt}{}{C_6H_5}{H}{>}C{<}\genfrac{}{}{0pt}{}{OH}{CH_2\cdot CO_2H}\ \begin{array}{l}\xrightarrow{\text{(by }PCl_5)}\ d\text{-}\genfrac{}{}{0pt}{}{C_6H_5}{H}{>}C{<}\genfrac{}{}{0pt}{}{Cl}{CH_2\cdot CO_2H}\\ \xrightarrow{\text{(by }SOCl_2)}\ l\text{-}\genfrac{}{}{0pt}{}{C_6H_5}{H}{>}C{<}\genfrac{}{}{0pt}{}{Cl}{CH_2\cdot CO_2H}\end{array}$$

With malic acid, however, both reagents cause a change of sign of rotation:



$$l\text{-}\genfrac{}{}{0pt}{}{CO_2H}{H}{>}C{<}\genfrac{}{}{0pt}{}{OH}{CH_2\cdot CO_2H}\ \xrightarrow[\text{(by }SOCl_2)]{\text{(by }PCl_5)}\ d\text{-}\genfrac{}{}{0pt}{}{CO_2H}{H}{>}C{<}\genfrac{}{}{0pt}{}{Cl}{CH_2\cdot CO_2H}\,.$$

Now, Pickard and Kenyon (T., 1911, **99**, 45) have prepared a number of haloids from the active alcohols by the action of halogen hydride, and in every case the formation of haloid was accompanied by a change of sign of rotation. Attempts to reconvert these haloids into the optically pure alcohols were unsuccessful; the values recorded for the haloids are undoubtedly too low, and the authors state that "the preparation of them with any degree of certainty that racemisation has been avoided is tedious." The action of hydrogen chloride at 0° on *d*-phenylmethylcarbinol led to the formation of a lævorotatory α-chloroethylbenzene with $[\alpha]_D^{17}\ -5{\cdot}8^\circ$. Pickard and Kenyon point out, however, in a recent communication (*Ber.*, 1912, **45**, 1592) that *sec.-d*-octyl alcohol is converted by hydrogen bromide into *sec.-l*-octyl bromide, from which the original alcohol can be regenerated by means of silver oxide and water.

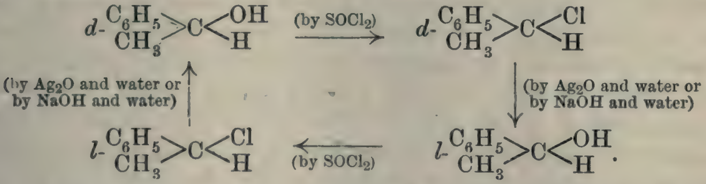
We find that phosphorus trichloride behaves like hydrogen chloride towards *d*-phenylmethylcarbinol; a change of sign of rotation occurs, the haloid having the value $[\alpha]_D^{18}\ -8{\cdot}1^\circ$. On the other hand, when thionyl chloride is employed, the sign of rotation is unchanged, and the resulting α-chloroethylbenzene has $[\alpha]_D\ +50{\cdot}6^\circ$. This is a very striking example of the fact that when the hydroxy-group in an optically active compound is displaced by the chlorine atom by the agency of thionyl chloride, the extent of the racemisation is much less than when the displacement is effected by other agents.

The action of acetyl chloride on the active phenylmethylcarbinols leads to the formation of α-chloroethylbenzene, the product having the same sign of rotation as the alcohol used as the starting point. We attach little importance to this observation, however, since the product may not be quite free from ester (see experimental part).

The displacement of chlorine in the active α-chloroethylbenzenes, formed by the interaction of thionyl chloride and the alcohols, was first of all effected by silver oxide and water. A change of sign of rotation occurred, the alcohol isolated from *d*-α-chloroethylbenzene, for example, having $[\alpha]_D$ −13·2°. Since the original *d*-phenylmethylcarbinol had $[\alpha]_D$ +43·4°, it will thus be seen that a considerable amount of racemisation had occurred during the displacement reactions. The extent of the racemisation is much more pronounced when the displacement of the chlorine is effected by aqueous sodium hydroxide. Here again a change of sign of rotation occurs, the resulting alcohol having only $[\alpha]_D$ about −1·7°.

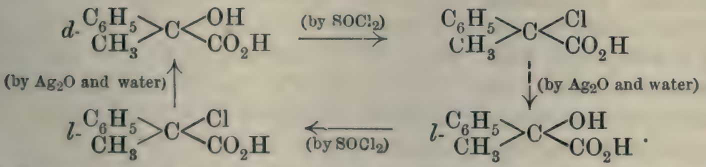
The displacement of chlorine by the hydroxy-group is attended by more racemisation in other cases also where aqueous sodium hydroxide is used in place of silver oxide and water. For example, the α-hydroxy-α-phenylpropionic acid, obtained from *l*-α-chloro-α-phenylpropionic acid by means of silver oxide and water, has $[\alpha]_D$ +9·4° in ethyl-alcoholic solution,* whereas racemisation is complete when aqueous sodium hydroxide is used (T., 1910, **97**, 1016).

The interconversion of the phenylmethylcarbinols can thus be brought about by the following cycle, which represents the first instance of the interconversion of enantiomorphously related alcohols by the Walden inversion:



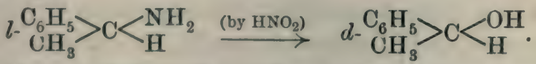
$$\begin{tikzcd} d\text{-}{C_6H_5 \atop CH_3}{>}C{<}{OH \atop H} \arrow[r, "\text{(by SOCl}_2\text{)}"] & d\text{-}{C_6H_5 \atop CH_3}{>}C{<}{Cl \atop H} \arrow[d, "\text{(by Ag}_2\text{O and water or by NaOH and water)}"] \\ l\text{-}{C_6H_5 \atop CH_3}{>}C{<}{Cl \atop H} \arrow[u, "\text{(by Ag}_2\text{O and water or by NaOH and water)}"] & l\text{-}{C_6H_5 \atop CH_3}{>}C{<}{OH \atop H}. \arrow[l, "\text{(by SOCl}_2\text{)}"'] \end{tikzcd}$$

It is interesting to note the close parallelism of these changes with the following undergone by the α-hydroxy-α-phenylpropionic acids:



$$\begin{tikzcd} d\text{-}{C_6H_5 \atop CH_3}{>}C{<}{OH \atop CO_2H} \arrow[r, "\text{(by SOCl}_2\text{)}"] & {C_6H_5 \atop CH_3}{>}C{<}{Cl \atop CO_2H} \arrow[d, "\text{(by Ag}_2\text{O and water)}"] \\ l\text{-}{C_6H_5 \atop CH_3}{>}C{<}{Cl \atop CO_2H} \arrow[u, "\text{(by Ag}_2\text{O and water)}"] & l\text{-}{C_6H_5 \atop CH_3}{>}C{<}{OH \atop CO_2H}. \arrow[l, "\text{(by SOCl}_2\text{)}"'] \end{tikzcd}$$

Reference may be made here to certain racemisation phenomena already recorded in the literature regarding the phenylmethylcarbinols. Marckwald and Meth (*Ber.*, 1905, **38**, 801) investigated the change:



$$l\text{-}{C_6H_5 \atop CH_3}{>}C{<}{NH_2 \atop H} \xrightarrow{\text{(by HNO}_2\text{)}} d\text{-}{C_6H_5 \atop CH_3}{>}C{<}{OH \atop H}.$$

and drew the conclusion, from the small rotatory power of the resulting alcohol, namely, $[\alpha]_D$ +2·7°, that partial racemisation had taken place. The same action was studied by Holmberg (*Ber.*, 1912,

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* *d*-α-Hydroxy-α-phenylpropionic acid has $[\alpha]_D$ +37·7°.

**45**, 997), who, being unacquainted with the work of Pickard and Kenyon (T., 1911, **99**, 45; compare also *Ber.*, 1912, **45**, 1592), was in error in supposing that he had obtained the optically pure alcohol. The following observations are recorded by Holmberg:

(1) Total racemisation occurred when a dextrorotatory phenylmethylcarbinol with $\alpha_D^{15}$ ($[\alpha]_D$?) $+5 \cdot 0°$ was acted on by hydrogen bromide.

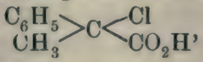
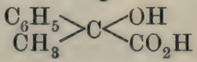
(2) A change of sign of rotation occurred when a lævorotatory phenylmethylcarbinol with $\alpha_D$ ($[\alpha]_D$?) $-4 \cdot 40°$ was acted on by phosphorus pentabromide.

(3) A change of sign of rotation occurred when a dextrorotatory $\alpha$-bromoethylbenzene with $\alpha_D^{20}$ ($[\alpha]_D^{20}$?) $+1 \cdot 37°$ was acted on by silver oxide and water.

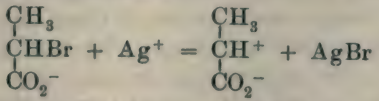
We also investigated the action of thionyl chloride on *d*-amyl alcohol, the lævorotatory constituent of fusel oil. Le Bel had shown many years ago that a change of sign of rotation occurred when this alcohol interacted with phosphorus pentachloride, and subsequent work has shown that derivatives of *d*-amyl alcohol are dextrorotatory. The amyl chloride obtained by means of thionyl chloride is also dextrorotatory; *d*-amyl chlorosulphinate was formed as an intermediate product, from which sulphur dioxide was readily eliminated by heating under the ordinary pressure. Thus the amyl chloride, obtained by the action either of phosphorus pentachloride or of thionyl chloride on the alcohol, is dextrorotatory, a result which was expected, since the hydroxy-group of the alcohol is not directly attached to the asymmetric carbon atom.

A contribution to the theoretical side of the problem of the Walden inversion has recently been published by Biilmann (*Annalen*, 1912, **388**, 330), who criticises adversely certain conceptions which had been previously advanced by E. Fischer (*ibid.*, 1911, **381**, 123; **386**, 374). To this criticism Fischer has replied (*ibid.*, 1912, **394**, 350). In addition to the points dealt with by Fischer, there are several aspects submitted by Biilmann with which we find ourselves unsympathetic, and we accordingly take the present opportunity of referring to these.

In the first place, the displacement of halogen by the hydroxy-group by the aid of silver oxide and water is discussed, the formation of lactic acid from optically active $\alpha$-bromopropionic acid being cited as a typical example. The suggestion is made that in such displacements the action is really one between water and silver salt, and, according to Biilmann, experimenters on the Walden inversion have failed to realise this. Biilmann has neglected to observe, however, that we have actually studied the action of water on silver salt in several instances; for example, it was pointed out

(T., 1908, **93**, 811) that silver *l*-phenylchloroacetate was prepared by the addition of silver nitrate to sodium *l*-phenylchloroacetate, and the sparingly soluble precipitate was separated. The action of water on it at the ordinary temperature was then examined, and contrasted with the action of water and silver carbonate on *l*-phenylchloroacetic acid; these two actions were similar in so far as a dextrorotatory mandelic acid was isolated in each case.* Moreover, in subsequent work we invariably recognised that the action of silver oxide (or silver carbonate) and water on a halogen substituted acid could anyhow be attended by the action of water on the silver salt.† There is little doubt, however, that in certain cases where silver oxide and water have been employed for the purpose of displacing halogen, the action is not simply one of water on silver salt, but is more complex. For instance, when *l*-*α*-chloro-*α*-phenylpropionic acid,  $\genfrac{}{}{0pt}{}{C_6H_5}{CH_3}\!>\!C\!<\!\genfrac{}{}{0pt}{}{Cl}{CO_2H}$, is shaken with water at the ordinary temperature, the chlorine is displaced with remarkable celerity, and the solution becomes optically inactive owing to the production of *r*-*α*-hydroxy-*α*-phenylpropionic acid,  $\genfrac{}{}{0pt}{}{C_6H_5}{CH_3}\!>\!C\!<\!\genfrac{}{}{0pt}{}{OH}{CO_2H}$; on the other hand, with silver oxide and water, a dextrorotatory *α*-hydroxy-*α*-phenylpropionic acid is formed from the *l*-chloro-acid (T., 1910, **97**, 1016). It is quite likely that two distinct actions are here proceeding concomitantly. Nevertheless, the possibility that the mechanism of the action of water on the chloro-acid is identical with that of the action of water on the silver salt of the chloro-acid must be admitted in some cases, and the kinetic studies of Senter and of Holmberg may be expected to throw much light on a problem of this nature.

According to Biilmann, no Walden inversion takes place when the halogen in an *α*-halogen acid is displaced by the hydroxy-group by means of silver oxide and water. The action is regarded as one of direct substitution, the silver salt being dissociated in aqueous solution, and the positive silver ion withdrawing the bromine to form undissociated haloid, thus:



$$\begin{array}{l}CH_3\\ |\\ CHBr\\ |\\ CO_2^-\end{array} + Ag^+ = \begin{array}{l}CH_3\\ |\\ CH^+\\ |\\ CO_2^-\end{array} + AgBr$$

(Optically active.) (Optically active.)

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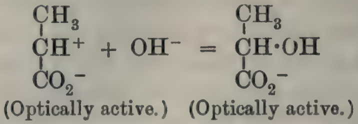
* Compare also the action of water on lead, ferric and mercurous *l*-phenylchloroacetates (T., 1909, **95**, 777), on silver *d*-*α*-bromo-*β*-phenylpropionate (T., 1910, **97**, 1355), and on silver *l*-dibromosuccinate (T., 1912, **101**, 1196).

† In practice, it is, as a rule, more convenient to conduct the displacement of halogen by means of silver oxide and water rather than to separate the silver salt and then act on it with water.

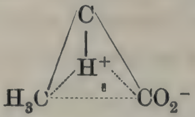
Then the "Zwitterion" combines with the negative hydroxy-ion of water to form an ion of lactic acid:



$$\begin{array}{c}CH_3\\|\\CH^+\\|\\CO_2^-\end{array} + OH^- = \begin{array}{c}CH_3\\|\\CH\cdot OH\\|\\CO_2^-\end{array}$$

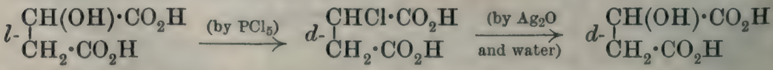
(Optically active.) (Optically active.)

Now, on the above representation the central carbon atom which was originally quadrivalent apparently ceases to have a tetrahedral environment, and, since a "Zwitterion" is supposed to be electrically neutral, it cannot even be urged that a free electric charge plays the part of the fourth grouping which is necessary for the retention of asymmetry. In order therefore to visualise a "Zwitterion" like that postulated above, which will preserve an enantiomorphous configuration after it has been formed from the active bromopropionic ion, it becomes necessary to imagine a grouping of this kind:



The carbon atom is here represented at the apex of a tetrahedron, and the three other groups at the corners. Surely, however, optical activity must vanish before a complex of this type can possess the free existence in solution, such as is tacitly implied by Biilmann for the "Zwitterion." Otherwise, the formation of an optically active structure containing an asymmetric tervalent carbon atom must be admitted, a view for which there is not the slightest experimental evidence. On these grounds, Biilmann's conception, however suggestive it may be, can hardly be accepted as tenable.

At least two separate displacement reactions are necessary for the proof of the occurrence of a Walden inversion; thus, with the interconversion of the phenylmethylcarbinols, we have (1) the displacement of the hydroxy-group by means of thionyl chloride, and (2) the elimination of chlorine in the resulting α-chloroethylbenzene. A configurational change occurs at one of these stages, but at which one it is at present impossible to assert with definiteness. It is, of course, true that in the earlier experimental work on the subject it was customary to regard as "normal" one of the displacement reactions involved, and the other as "abnormal." For example, in the changes examined by Walden:



$$l\text{-}\begin{array}{l}CH(OH)\cdot CO_2H\\|\\CH_2\cdot CO_2H\end{array} \xrightarrow{\text{(by PCl}_5\text{)}} d\text{-}\begin{array}{l}CHCl\cdot CO_2H\\|\\CH_2\cdot CO_2H\end{array} \xrightarrow[\text{and water)}]{\text{(by Ag}_2\text{O}} d\text{-}\begin{array}{l}CH(OH)\cdot CO_2H\\|\\CH_2\cdot CO_2H\end{array}$$

the action of phosphorus pentachloride was designated as "normal," that is, unaccompanied by configurational change, whereas the action of water and silver oxide was called "abnormal." When, however, the experimental data of the past few years are carefully reviewed, it must be conceded that, in practically every case, it is impossible to fix a Walden inversion as occurring definitely during any single displacement reaction (compare Fischer, *loc. cit.*). This is not, however, the conclusion which is arrived at by Biilmann, who submits the following generalisations:

(1) The action of water on optically active silver salt is one of direct displacement, "Stellvertretung' (or, to use the old term, is "normal"), since it occurs between the cation and halogen.

(2) The action of nitrous acid on active amino-acids is one of direct displacement.

(3) The action of phosphorus pentachloride on active hydroxy-acids involves a configurational change.

(4) The action of sodium hydroxide or of ammonia on an active halogen acid involves a configurational change.

These ideas are unfortunate, as they are not in accordance with the facts.

Biilmann (*loc. cit.*, p. 335) writes as follows: "Vorausgeschickt sei die Bemerkung, dass das experimentelle Material, welches besonders E. Fischer und Walden in den letzten 14 Jahren gebracht haben, so vorzüglich es auch in anderer Hinsicht sein mag, doch so wenig einheitlich ist, dass eine exakte Behandlung der Frage ohne Zweifel eine Neubearbeitung fordern wird. Selbst in den drei Gruppen, wo das Material am wenigsten Lücken zeigt, der Alaningruppe, der Asparaginsäure und der Valingruppe, gilt dieser Einwand gegen die Einheitlichkeit." There is, however, a fourth group, namely, the mandelic acid group, which has been investigated with some degree of completeness in this laboratory. Had Biilmann been cognisant of the work in this branch, he would doubtless have recognised that the above-mentioned views cannot be entertained. In this connexion it will suffice to refer to two methods by which the active mandelic acids can be interconverted.

The following transformations can be effected:

$$\begin{tikzcd}
d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[r, shift left, "\text{(by PCl}_5\text{)}"] & l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[l, shift left, "\text{(by Ag}_2\text{O and water)}"] \arrow[d, "\text{(by NaOH and water)}"] \\
d\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[u, "\text{(by NaOH and water)}"] \arrow[r, shift right, "\text{(by Ag}_2\text{O and water)}"'] & l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[l, shift right, "\text{(by PCl}_5\text{)}"']
\end{tikzcd}$$

If the first of Biilmann's theses be accepted, then the *l*-chloro-acid passes into *d*-mandelic acid without configurational change; but then the action of phosphorus pentachloride on *d*-mandelic acid ought, according to Biilmann, to give *d*-chloro-acid, which it does not. If therefore Biilmann's first thesis (regarding the action of water on silver salt) is correct, his third thesis (regarding the action of phosphorus pentachloride) is incorrect, and vice versa. Also, if, in the above cycle, Biilmann's third thesis is accepted, then his fourth thesis (regarding the action of sodium hydroxide) is invalid, and vice versa.

The following cycle can also be experimentally realised:

$$\begin{tikzcd}
d\text{-}C_6H_5{\cdot}CH(OH){\cdot}CO_2H \arrow[d, "\text{(by PCl}_5\text{)}"'] & l\text{-}C_6H_5{\cdot}CH(NH_2){\cdot}CO_2H \arrow[l, "\text{(by HNO}_2\text{)}"'] \\
l\text{-}C_6H_5{\cdot}CHCl{\cdot}CO_2H \arrow[d, "\text{(by NH}_4\text{OH)}"'] & d\text{-}C_6H_5{\cdot}CHCl{\cdot}CO_2H \arrow[u, "\text{(by NH}_4\text{OH)}"'] \\
d\text{-}C_6H_5{\cdot}CH(NH_2){\cdot}CO_2H \arrow[r, "\text{(by HNO}_2\text{)}"'] & l\text{-}C_6H_5{\cdot}CH(OH){\cdot}CO_2H \arrow[u, "\text{(by PCl}_5\text{)}"']
\end{tikzcd}$$

It will be seen that these results are also in disagreement with Biilmann's views.

## EXPERIMENTAL.

### *Action of Thionyl Chloride on the Active Phenylmethylcarbinols.*

*d*-Phenylmethylcarbinol was prepared by the resolution of the hydrogen succinic *dl*-ester by means of brucine (Pickard and Kenyon, T., 1911, **99**, 45). It boiled at 104°/23 mm., and had $[\alpha]^{20}_{D}$ + 43·4°, values in satisfactory agreement with those quoted by Pickard and Kenyon.

When the *d*-alcohol (4 grams) was added gradually to thionyl chloride (10 grams), there was no pronounced rise of temperature, although the action was vigorous after each addition. After fifteen minutes at the ordinary temperature, the liquid was distilled under diminished pressure. Yield, 4 grams.

d-*α-Chloroethylbenzene*, $C_6H_5{\cdot}CHCl{\cdot}CH_3$, is an oil which boils at 85°/20 mm.

Found, Cl = 25·3 (by Stepanow's method). Calc., Cl = 25·2 per cent.

It had $\alpha^{20}$ + 26·90° in a 50 mm. tube; $d^{20}_{4}$ 1·0631; whence $[\alpha]^{20}_{D}$ + 50·6°.

Although it was anticipated, in the light of previous experience in displacement reactions, that some racemisation would accompany the substitution of the hydroxy-group in *d*-phenylmethylcarbinol by a chlorine atom, there is no proof that any such phenomenon had occurred in the present instance. On the contrary, it is permissible to draw the conclusion that the above-mentioned chloro-substitution product can contain only very little of the *dl*-form. In the event of racemisation accompanying the displacement, it is extremely probable that the chloroethylbenzene, obtained from different preparations by the agency of thionyl chloride, would not always possess the same rotatory power. It was found, however, in a second experiment, where 5 grams of the *d*-alcohol and 15 grams of thionyl chloride were employed, that the resulting chloroethylbenzene had $\alpha_D$ +26·85° in a 50 mm. tube.

The *l*-alcohol was not prepared in the pure state, but a product with a fairly high rotation was obtained from the mother liquors resulting from the crystallisation of the brucine salt of the hydrogen succinic *d*-ester. Forty-one grams of this product, which had $\alpha_D$ −26·70° in a 1-dcm. tube, were added as before to 56 grams of thionyl chloride. The resulting α-chloroethylbenzene boiled at 85°/20 mm., and had $\alpha_D^{20}$ −32·05° ($l=1$), $d_4^{20}$ 1·0632; whence $[\alpha]_D^{20}$ −30·1°. (Found, Cl = 25·3. Calc., Cl = 25·2 per cent.) In a similar manner, the chloroethylbenzene, prepared from a lævorotatory alcohol with $\alpha_D$ −29·0° ($l=1$), had $\alpha_D$ −33·20° ($l=1$).

### *Action of Phosphorus Trichloride on the Active Phenylmethylcarbinols.*

Phosphorus trichloride (20 grams) was cooled to 0°, and the *d*-alcohol (5 grams) was added drop by drop. The product was fractionated, and the portion boiling at 80—80·5°/15 mm. was collected, and found to be lævorotatory with $\alpha_D^{18}$ −4·32° ($l=0·5$), $d_4^{18}$ 1·0638; whence $[\alpha]_D^{18}$ −8·1°. Found, Cl = 25·1. Calc., Cl = 25·2 per cent.

This change of sign of rotation was confirmed by the action of phosphorus trichloride (20 grams) on a lævorotatory phenylmethylcarbinol (5 grams), having $\alpha_D$ −32·0° ($l=1$). The chloroethylbenzene amounted to 3 grams, and had $\alpha_D$ +2·95° ($l=0·5$). Found, Cl = 25·1. Calc., Cl = 25·2 per cent.

The action of phosphorus pentachloride on the alcohols led to the formation of viscid oils containing phosphorus, and was not therefore thoroughly investigated.

### *Action of Acetyl Chloride on the Active Phenylmethylcarbinols.*

The behaviour of acetyl chloride towards *d*-phenylmethylcarbinol was studied in consequence of an observation made by Radziszewski (*Ber.*, 1874, **7**, 140), who added the optically inactive alcohol to an excess of acetyl chloride and found that, when the product, which consisted mainly of acetic acid and α-chloroethylbenzene, was treated with silver acetate, it gave the ester derived from phenylmethylcarbinol. α-Chloroethylbenzene was not, however, isolated by Radziszewski in the course of his examination of this action.

Five grams of *d*-phenylmethylcarbinol were added drop by drop during fifteen minutes to 20 grams of acetyl chloride, the liquid being kept cold. After thirty minutes at the ordinary temperature, the oil was distilled. The fraction boiling at 80—81°/15 mm. amounted to 3·7 grams, and was dextrorotatory, having $\alpha_D$ +0·95° in a 50 mm. tube. This liquid was warmed at 40° for ten minutes with 5 grams of acetyl chloride, and again distilled. The activity of the fraction boiling at 80—80·5°/15 mm. was practically the same as before, the value obtained being $\alpha_D$ +0·90° in a 50 mm. tube. It is possible, however, that a trace of ester may have been present even after this treatment. The value for the density, namely, $d_4^{20}$ 1·061, is rather low, and the analysis was not very satisfactory. Found, Cl=24·7. Calc., 25·2 per cent.

A similar result was arrived at when the lævorotatory alcohol was examined from the same standpoint. Ten grams of an alcohol with $\alpha_D$ −20·6° ($l$=1) were added to 20 grams of acetyl chloride during half an hour. After fractionation, 6 grams of an oil boiling at 85°/20 mm. were collected, having $d_4^{18}$ 1·059. On polarimetric examination, the product was found to be lævorotatory, giving $\alpha_D$ −0·73° in a 50 mm. tube. Found, Cl=24·8. Calc., Cl=25·2 per cent.

### *Action of Silver Oxide and Water on the Active α-Chloroethylbenzenes.*

Six grams of the partly racemised α-chloroethylbenzene with $[\alpha]_D^{20}$ −30·1° were added to 60 c.c. of water, and the mixture shaken with silver oxide (6 grams) for two hours, and then heated on the water-bath for fifteen minutes. The alcohol was separated by distillation in steam, extracted with ether, and fractionated under ordinary pressure. The portion boiling at 196° to 200° (2 grams) had $\alpha_D^{17}$ +3·71° ($l$=0·5), $d_D^{17}$ 1·0135; whence $[\alpha]_D^{17}$ +7·3°. Found, C=78·0; H=8·5. Calc., C=78·6; H=8·3 per cent.

A change of sign of rotation had thus been effected by the displacement of the chlorine atom in *l*-α-chloroethylbenzene by the hydroxy-group, and it was also obvious that a considerable amount of racemisation had occurred.

The resulting alcohol with $[\alpha]_D$ +7·3° was added to an equal weight of phenylcarbimide, and warmed gently. After twenty-four hours, the crystals of the phenylurethane were removed and washed with light petroleum. Their solution in benzene was dextrorotatory:

$$l=2;\ c=5{\cdot}015;\ \alpha_D\ +1{\cdot}61°;\ [\alpha]_D\ +16{\cdot}1°.$$

(Found, C=74·2; H=6·3. Calc., C=74·6; H=6·3 per cent.)

When this product was crystallised from light petroleum, the optically active phenylurethane tended to accumulate in the filtrate; thus, after one crystallisation, the crystals had $[\alpha]_D$ +6·1° in benzene solution, and after a further crystallisation, the activity had diminished to $[\alpha]_D$ +1·3°. The melting point at this stage was 91—93°, whereas the phenylurethane of *dl*-phenylmethylcarbinol melts at 94° according to Klages and Allendorff (*Ber.*, 1898, **31**, 1004).

The *phenylurethane* of d-*phenylmethylcarbinol* was prepared from the pure alcohol, and crystallised from light petroleum, from which it separates in glassy needles, m. p. 99°:

0·2036 gave 0·5535 $CO_2$ and 0·115 $H_2O$. C=74·1; H=6·3.
$C_{15}H_{15}O_2N$ requires C=74·6; H=6·3 per cent.

A determination of its specific rotation was made in benzene solution:

$$l=2;\ c=4{\cdot}864;\ \alpha_D^{16}+9{\cdot}87^\circ;\ [\alpha]_D^{16}\ +101{\cdot}5^\circ.$$

It is accordingly possible to prepare a mixture of the *r*- and *d*-phenylurethanes from *l*-phenylmethylcarbinol, but, unless the *d*-phenylurethane preponderated in the mixture, its isolation by crystallisation could not readily be effected.

Nine grams of *d*-*α*-chloroethylbenzene with $\alpha_D^{18}$ +26·85° (*l*=0·5), prepared from *d*-phenylmethylcarbinol, were added to 90 c.c. of water, and the mixture shaken on the machine for two hours with the silver oxide prepared by the action of baryta on 17 grams of silver nitrate. The alcohol was isolated by steam distillation, etc. The fraction boiling at 198—201° amounted to 4·4 grams. (Found, C=78·4; H=8·4. Calc., C=78·6; H=8·3 per cent.) The alcohol consisted of a mixture of *l*- and *dl*-phenylmethylcarbinols. The following observations were made:

$$l=1;\ \alpha_D^{20}-13{\cdot}32^\circ;\ d_4^{20}\ 1{\cdot}0118;\ [\alpha]_D^{20}-13{\cdot}2^\circ.$$

Two grams were converted into the phenylurethane, and the resulting solid crystallised from light petroleum, and then examined polarimetrically in benzene solution:

$$l=2;\ c=7{\cdot}2;\ \alpha_D-3{\cdot}22^\circ;\ [\alpha]_D-22{\cdot}4^\circ.$$

After an additional crystallisation from light petroleum, the mixture contained a less proportion of the active phenylurethane than before, the specific rotatory power being −17·6° for *c*=7·12. An analysis was made of the less active mixture. (Found, C=74·7; H=6·3. Calc., C=74·6; H=6·3 per cent.)

### *Action of Sodium Hydroxide and Water on the Active α-Chloroethylbenzenes.*

Six grams of the partly racemised α-chloroethylbenzene with $[\alpha]_D^{20}$ −30·1° were boiled for two hours with a solution of 6 grams of sodium hydroxide in 60 c.c. of water. The alcohol was obtained as usual. The fraction boiling at 196—200° (2 grams) was dextrorotatory, having $\alpha_D$ +0·65° ($l$=0·5).

(Found, C=77·8; H=8·3. Calc., C=78·6; H=8·3 per cent.)

The mixture of the *d*- and *r*-phenylurethanes was made as before. The crude product had $[\alpha]_D$ +0·95° in benzene solution, and became quite inactive after one crystallisation.

Nine grams of *d*-α-chloroethylbenzene were boiled for three hours with a solution of 9 grams of sodium hydroxide in 90 c.c. of water. The yield of alcohol boiling at 197—200° amounted to 2·5 grams. The liquid was lævorotatory, giving $\alpha_D$ −0·85° ($l$=0·5). The phenylurethane prepared from it had $[\alpha]_D$ −1·15° in benzene solution, and, after one crystallisation from light petroleum, it was inactive. (Found, C=74·8; H=6·3. Calc., C=74·6; H=6·3 per cent.)

The displacement of chlorine by the hydroxy-group was also effected in the following manner. Ten grams of the lævorotatory α-chloroethylbenzene with $[\alpha]_D^{20}$ −30·1° were dissolved in 30 c.c. of glacial acetic acid, and shaken for an hour with 15 grams of silver acetate. The mixture was finally heated on the water-bath. The silver chloride was removed, and the acetic acid distilled off under diminished pressure, and then the acetate was distilled. The acetate was saponified, the resulting alcohol was distilled in a current of steam, and isolated in the customary manner. Five grams were obtained with b. p. 196—197° and $\alpha_D$ +1·60° in a 50 mm. tube.

### *Action of Thionyl Chloride on* d-*Amyl Alcohol.*

The method of Marckwald and McKenzie (*Ber.*, 1901, **34**, 485) was employed for the preparation of *d*-amyl alcohol. The product contained, however, a little of the isomeric *iso*amyl alcohol, since its specific rotatory power was −5·7°, whereas the pure alcohol has $[\alpha]_D$ −5·9°. Twelve grams were gradually added to 30 grams of thionyl chloride, and, after one hour, the liquid was distilled under diminished pressure. The yield of the chlorosulphinate was 22 grams.

d-*Amyl chlorosulphinate*, $C_5H_{11}O\cdot SOCl$, is a colourless oil with a pungent odour, and boils at 73°/15 mm. It fumes slightly when exposed to air, and is readily decomposed by water:

Found, $SO_2 = 37{\cdot}3$; $Cl = 20{\cdot}7$.

$C_5H_{11}O_2ClS$ requires $SO_2 = 37{\cdot}6$; $Cl = 20{\cdot}8$ per cent.

It had $\alpha_D^{14\cdot5}$ +4·87° ($l = 1$); $d_4^{14\cdot5}$ 1·1399; whence $[\alpha]_D^{14\cdot5}$ +4·3°.

In a second preparation, a compound with the same rotatory power as the preceding was obtained. The rotatory power is not diminished when the sulphinate is redistilled under diminished pressure.

*d*-Amyl chlorosulphinate (22 grams) was heated at 120° for two hours under the ordinary pressure. Sulphur dioxide was evolved. The residue was distilled, and the product, boiling at 98—99°, collected. Yield, 12 grams.

d-*Amyl chloride* is a colourless liquid, boiling at 98—99°. It has $\alpha_D^{15}$ +0·75° ($l = 0{\cdot}5$); $d_4^{15}$ 0·8868; whence $[\alpha]_D^{15}$ +1·7°.

In another preparation the value $\alpha_D^{18}$ +2·93° in a 2-dcm. tube was obtained; these values agree. The rotation was not altered by redistillation:

0·1488 gave 0·1995 AgCl. $Cl = 33{\cdot}2$.

$C_5H_{11}Cl$ requires $Cl = 33{\cdot}3$ per cent.

The value quoted by Le Bel (*Bull. Soc. chim.*, 1876, [ii], **25**, 545) for *d*-amyl chloride is $[\alpha]_D$ +1·24°. The haloid was prepared by Le Bel by the interaction of phosphorus pentachloride and a highly active amyl alcohol, but the preparation appears to have been attended with some racemisation.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

BIRKBECK COLLEGE,
LONDON, E.C.

# ANNUAL GENERAL MEETING,

MARCH 14TH 1913.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,
in the Chair.

Mr. C. H. HAMPSHIRE and Mr. T. R. MERTON were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society from January, 1912, to date, and a statement was made by the TREASURER as to the Income and Expenditure for 1912. The adoption of the Report of the Council, together with the Balance Sheet and Statement of Accounts for the year ended December 31st, 1912, was proposed by Mr. T. FAIRLEY, seconded by Professor A. G. GREEN, and carried unanimously.

A Vote of Thanks to the Auditors was proposed by the TREASURER, seconded by Dr. S. B. SCHRYVER, and acknowledged by Professor J. M. THOMSON.

## REPORT OF COUNCIL, 1912—1913.

THE Annual Reports of the Council have, in the past, dealt with the work of the Society during the previous calendar year, but the general portion of the present Report refers to the period from the commencement of 1912 to March, 1913, and this portion of future Reports will concern the period from one Annual General Meeting to the next Annual General Meeting.

On the 31st December, 1911, the number of Fellows was 3,104. During 1912, 184 Fellows were elected, and 7 have been reinstated, the gross total being 3,295. The Society has lost 33 Fellows by death, 52 have resigned, 1 has been elected an Honorary and Foreign Member, the elections of 4 Fellows have become void, and 47 Fellows have been removed for non-payment of Annual subscriptions.

The total number of Fellows, therefore, on the 31st December, 1912, was 3,158, showing a net increase of 54 over the preceding year. The number of Fellows elected during 1912 exceeds the average for the past six years by 21 Fellows, and the small net increase in the number of Fellows is accounted for by the large number of resignations and of Fellows removed for non-payment of Annual Subscriptions.

The names of the deceased Fellows, with the dates of their election, are:

George Attwood (1872).
Alfred Edward Beanes (1902).
Andrew Heggie Black (1879).
Robert Holford Macdowall Bosanquet (1865).
John Macdonald Cameron (1875).
Miles Coupe (1905).
Edward Divers (1860).
Arthur Edward Ekins (1883).
Algernon John Elkington (1911).
John Oliver Ferrier (1902).
Angus Fraser (1867).
Thomas Griffiths (1879).
Alexander Hill (1882).
Reginald Howell (1880).
Otis Coe Johnson (1897).
Humphrey Owen Jones (1900)
David Skinner Kemp (1867).
William Frederick Laycock (1890).
Theodore David Lichtenstein (1878).
Charles William Low (1884).
John McArthur (1887).
William Masters (1873).
Henry de Mosenthal (1890).
Benjamin Edward Reina Newlands (1864).
John Pattinson (1863).
B. Venkata Rao (1911).
Arthur Richardson (1883).
Henry Salt (1863).
Henry Seward (1870).
William Robert Rigg Starling (1906).
James Pim Strangman (1887).
John Wade (1890).
William Ord Wootton (1908).

The following Fellows have resigned:

James Henry Allan.
Allan Baguley.
John Augustus Hermann Brincker.
Arthur Brooke.
John Coggin Brown.
John Arthur Carpenter.
William Clacher.
George Bertram Cockburn.
William Cormack.
Samuel Herbert Cox.
William Salvador Curphey.
Frederick Davis.
Henry Wilson Davis.
Arthur William Eastwood.
Vincent Edwards.
Nevil Norton Evans.
John Edwin Farmer.
Reginald Williams Ferguson.
John Thomas Fox.
Gilbert Gunn.
Thomas Hartley.

William Pellew Harvey.
Alfred Kirby Huntington.
George Washington Kilner.
Stephen Joshua Lett.
Arthur Thomas McDougall.
Antholl Francis McEwen.
Alwyne Harcourt Meade.
Frederick Norton Kay Menzies
Christian Müller.
Herbert Simpson Newbould.
Frederick Norrington.
Robert Cecil Owen.
Herbert Spindler Pullar.
William Ralston.
John Armstedt Ray.
David Gibson Riddick.
James Beglar Robinson.
John Robinson.
Francis Murray Rogers.
William Saunders.
Alfred Henry Scholefield.
Frederick William Skirrow.
Henry George Stacey.
Samuel Stansfield.
William Scott Tebb.
John Traquair.
Stephen Herbert Trimen.
Herbert Wood Watson.
Thorp Whitaker.
*Frederick Louis Wilder.
William Arthur Reginald Wilks.

* Since reinstated

At the end of 1911 the number of Honorary and Foreign Members was 31. Since that date the Society has mourned the loss of Lecoq de Boisbaudran and J. W. Mallet, whilst on March 7th, 1912, P. A. Guye, T. B. Osborne, P. Walden, and R. Willstätter were elected. The total number of Honorary and Foreign Members, therefore, at the present time is 33.

The Council has great pleasure in offering hearty congratulations to the following, who, in 1912, attained their Jubilee as Fellows:

William Esson, elected May 1st, 1862.
William Adam Dixon, elected Dec. 18th, 1862.
Edmund James Mills, elected Dec. 18th, 1862.

The Council desires to record its high appreciation of the services rendered to the Society over a period of eight years by the retiring Senior Secretary, Professor Crossley. Professor Crossley's tenure of this arduous office has been distinguished by great administrative skill, by sound judgment, and by unfailing tact. The Society is deeply indebted to him for the generous manner in which he has placed his time and energies at its disposal.

During the year, 336 scientific communications were made to the Society, 256 of which have been published already in the Transactions, and abstracts of all have appeared in the Proceedings.

The volume of Transactions for 1912 contains 2,568 pages, of which 2,431 are occupied by 266 memoirs, the remaining 137 pages being devoted to the Obituary Notices, the Becquerel, Cannizzaro, and Moissan Memorial Lectures, the Report of the International

Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 259 memoirs which occupy 2,270 pages.

The Journal for 1912 contains 5,497 abstracts, which extend to 2,264 pages, whilst the abstracts for 1911 numbered 5,236, and occupied 2,200 pages. The abstracts may be classified as follows:

| | Pages. | No. of Abstracts. |
|---|---|---|
| PART I. | | |
| Organic Chemistry ........................ | 1,044 | 1,796 |
| PART II. | | |
| General and Physical Chemistry ......... | | 1,238 |
| Inorganic Chemistry ........................ | | 493 |
| Mineralogical Chemistry .................. | | 120 |
| Physiological Chemistry .................. | | 737 |
| Chemistry of Vegetable Physiology and Agriculture ........................... | | 385 |
| Analytical Chemistry ............. ......... | | 728 |
| | 1,220 | 3,701 |
| Total in Parts I. and II ........... | 2,264 | 5,497 |

The possibility of Fellows resident abroad procuring through the Society fuller abstracts of papers than appear in the Journal has been under consideration, and the Council has decided:

"That persons requiring expanded Abstracts or translations of papers published in other Journals should apply to the Editor. Ten shillings per printed page (about 500 words) will be charged, and payment should be made to the Editor at the time the request for a translation or fuller abstract is forwarded to him."

The Council has also resolved:

"That in order to obtain a more equal division of abstracts, those of Physiological Chemistry and the Chemistry of Vegetable Physiology and Agriculture shall, in future, be included in Part I. of the Abstracts, instead of in Part II."

Volume V. of the Collective Index of the Journal and Proceedings of the Chemical Society (1903—1912) will be issued in two parts: Part I (Author Index) in 1913, and Part 2 (Subject Index) in 1914. Such prompt publication of the Collective Index is rendered possible by the system employed for the preparation of the

Annual Indexes, as the work done in connection with the latter can be largely utilised for the Collective Index.

The Transactions for 1912 contain Obituary Notices of Walthère Spring and Louis Joseph Troost, Honorary and Foreign Members. Obituary Notices also appear of John Attfield, John Muter, and Nevil Story-Maskelyne, and the Council expresses its thanks to those gentlemen who have kindly prepared these notices.

The Society was represented at the funeral of the late Lord Lister by the President.

Since the last Report was published, the Society has had the privilege of listening to an account of the life and work of:

(*a*) S. Cannizzaro, from Sir William Tilden.
(*b*) H. Moissan, from Sir William Ramsay.
(*c*) H. Becquerel, from Sir Oliver Lodge.

The Council has considered the desirability of issuing a second volume of Memorial Lectures, and has decided to postpone the publication until after the delivery of the Ladenburg Lecture by Prof. Kipping and the Van't Hoff Lecture by Prof. James Walker, both of which lectures, it is hoped, will be delivered before the close of the present Session.

The President, Professor P. F. Frankland, was the official representative of the Society at the celebration, in July, 1912, of the 250th Anniversary of the Foundation of the Royal Society, when an address of congratulation was presented on behalf of the Chemical Society. The text of the address appeared in the Proceedings, Vol. 28, p. 248.

The Eighth International Congress of Applied Chemistry held in Washington and New York in September, 1912, was attended by Dr. M. O. Forster, Sir William Ramsay, and Sir Boverton Redwood as delegates of the Chemical Society.

The Society was represented at the Centenary Anniversary of the Academy of Natural Sciences of Philadelphia in March, 1912, by the late Professor J. W. Mallet and by Professor Alexander Smith; at the Bicentenary Festival of the Medical School, Trinity College, Dublin, in July, 1912, by Professor G. T. Morgan; and at the 25th Anniversary Celebration of the Verein Deutscher Chemiker by Dr. R. Messel.

During the Summer Vacation of 1912 the Society's Rooms were redecorated throughout. After consultation with the architect originally responsible for the scheme of ventilation in the Meeting Room, the Council also decided to place a large suction-fan in the roof over the Library, directly connected with the ventilating flues of the Meeting Room. This has had the result of materially improving the atmosphere of the room.

A conference of representatives of those Chemical Societies in Great Britain publishing abstracts of papers appearing in other Journals is taking place, at the suggestion of the Council, to consider the possibility of decreasing the cost of production of such abstracts. Delegates have been appointed by the various Societies as follows:

*Society of Chemical Industry.*—R. Messel, J. Lewkowitsch.

*Society of Public Analysts.*—L. Archbutt, H. D. Richmond, O. Hehner.

*Institute of Brewing.*—J. L. Baker, A. R. Ling.

*Institute of Metals.*—W. Rosenhain, G. S. Scott.

*Society of Dyers and Colourists.*—E. Knecht, W. M. Gardner.

*Iron and Steel Institute.*—J. E. Stead, G. C. Lloyd.

The Council Meetings of the International Association of Chemical Societies held in Berlin in April, 1912, were attended by the three representatives of the Society, Professor A. W. Crossley, Professor P. F. Frankland, and Sir William Ramsay, and an account of the work of the Council appeared in the Proceedings for 1912 (p. 201). The General Expenses of the Association for the previous year amounted to £60, of which sum the share of the Chemical Society was £10 6*s*. 7*d*.

The next meetings of the Council will be held in London during September, 1913, and the Officers of the Association are:

Sir William Ramsay, *President.*
Prof. Percy F. Frankland, *Vice-President.*
Prof. Arthur W. Crossley, *General Secretary.*

who remain in office until the end of the meeting.

The Society has received through Sir Edward Thorpe the Annual Report of the International Committee on Atomic Weights, 1913, together with a Table of Atomic Weights. The Report appears in the Proceedings, p. 213, and in the Transactions, p. 1829.

The Council has made a further donation of £10 to the International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological.

In the last report it was mentioned that it was proposed to raise a Memorial to the late Prof. J. H. van't Hoff, and that subscriptions would be received by the Treasurer. The sum of £65 4*s*. was subscribed by Fellows and forwarded to the Memorial Committee.

The Council has considered a request from the Director of the Municipal Laboratory of Paris for permission to arrange for the preparation of a French translation of the Annual Reports, and has agreed to the proposition. The publication of the work will be carried out by Messrs. Hermann et Fils, of Paris.

## INCOME AND EXPENDITURE ACCOUNT

*Income.*

| | | £ s. d. | £ s. d. |
|---|---|---|---|
| To Life Compositions | | | 386 0 0 |
| ,, Admission Fees | | | 692 0 0 |
| ,, Annual Subscriptions— | | | |
| Received in advance, on account of 1912 | | 232 0 0 | |
| ,, during 1912 ,, 1912 | | 4471 0 0 | |
| ,, ,, ,, ,, 1911 | | 354 0 0 | |
| ,, ,, ,, ,, 1905–10 | | 18 0 0 | |
| | | 5075 0 0 | |
| *Less* amount included in last year's Income, being valuation of Arrears as per last Balance Sheet | | 360 0 0 | |
| | | 4715 0 0 | |
| *Add* Arrears at date: 1912 £448; 1911 £30; 1910 £15, estimated to realise as per Balance Sheet | | 350 0 0 | |
| | | | 5065 0 0 |
| ,, Lady Subscribers | | | 6 0 0 |
| ,, Investments:— | | | |
| Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock | | 221 16 4 | |
| ,, £1050 London and North Western Railway 3 per cent. Debenture Stock | | 29 13 2 | |
| ,, £1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock | | 42 19 4 | |
| ,, £1400 India 2½ per cent. Stock | | 32 19 4 | |
| ,, £2400 Bristol Corporation 2½ per cent. Debenture Stock | | 56 10 0 | |
| ,, £4341 Midland Railway 2½ per cent. Preference Stock | | 102 3 10 | |
| ,, £1200 Leeds Corporation 3 per cent. Stock | | 33 18 0 | |
| ,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53 | | 42 7 6 | |
| ,, £1200 North British Railway 3 per cent. Debenture Stock | | 33 18 0 | |
| ,, £700 Canada 3½ per cent. Stock 1930/50 | | 23 1 6 | |
| ,, Income Tax Recovered | | 36 13 10 | |
| ,, Interest on Deposit Account | | 16 16 8 | |
| | | | 672 17 6 |
| ,, Publications:— | | | |
| Sales: | | | |
| Journals | | 916 17 6 | |
| Proceedings | | 47 14 9 | |
| General Index | | 20 6 0 | |
| Library Catalogue | | 1 7 0 | |
| List of Fellows | | 4 0 0 | |
| Atomic Weight Tables | | 0 9 2 | |
| Jubilee Volume | | 0 5 6 | |
| Annual Reports on Progress of Chemistry | | 185 8 11 | |
| | | 1176 8 10 | |
| *Less* Publishers' Commission | | 108 17 9 | |
| | | 1067 11 1 | |
| ,, Proceeds of Advertisements in Journal | £20 16 10 | | |
| *Less* Commission | 13 10 10 | | |
| | | 192 6 0 | |
| | | | 1259 17 1 |
| ,, Sale of Waste-paper, etc. | | | 2 13 2 |
| ,, Subscriptions from other Societies:— | | | |
| Society of Chemical Industry | | 9 9 0 | |
| Society of Public Analysts | | 11 0 6 | |
| Optical Society | | 10 10 0 | |
| British Science Guild | | 4 4 0 | |
| Institute of Chemistry | | 1 1 0 | |
| | | | 36 4 6 |
| | | | £8120 12 3 |

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

23, Queen Victoria Street, E.C.
*3rd March*, 1913.

W. B. KEEN,
*Chartered Accountant.*

## FOR THE YEAR ENDED 31ST DECEMBER, 1912.

### *Expenditure.*

| | £ | *s.* | *d.* | £ | *s* | *d.* |
|---|---|---|---|---|---|---|
| **By Expenses on account of Journal and Proceedings:—** | | | | | | |
| Salary of Editor, including Indexing | 570 | 0 | 0 | | | |
| Salary of Sub-Editor | 200 | 0 | 0 | | | |
| Editorial Postages | 31 | 1 | 4 | | | |
| Abstractors' Fees | 546 | 10 | 3 | | | |
| Printing of Journal | 2953 | 10 | 1 | | | |
| Banding | 60 | 15 | 8 | | | |
| Printing of Advertisements | 52 | 2 | 6 | | | |
| Wrappers and Addressing | 119 | 19 | 5 | | | |
| Distribution of Journal | 628 | 13 | 4 | | | |
| Authors' Copies | 192 | 19 | 5 | | | |
| Insurance of Stock at Clay's | 6 | 4 | 3 | | | |
| Printing of Proceedings | 218 | 12 | 5 | | | |
| Banding ,, | 8 | 14 | 8 | | | |
| Distribution ,, | 44 | 9 | 3 | | | |
| | | | | 5633 | 12 | 7 |
| ,, **Annual Reports on the Progress of Chemistry** | | | | 415 | 6 | 0 |
| ,, **Purchase of back numbers of Journal** | | | | 7 | 12 | 1 |
| ,, **List of Fellows** | | | | 72 | 7 | 9 |
| ,, **Library Expenses:—** | | | | | | |
| Salary of Librarian and Assistant | 190 | 12 | 0 | | | |
| Books and Periodicals | 246 | 12 | 3 | | | |
| Binding | 25 | 4 | 7 | | | |
| Bookcases | 14 | 19 | 4 | | | |
| | | | | 477 | 8 | 2 |
| ,, **Indexing for International Catalogue** | | | | 30 | 0 | 0 |
| ,, Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological | | | | 10 | 0 | 0 |
| ,, **International Association of Chemical Societies** | | | | 10 | 6 | 7 |
| ,, **Administrative Expenses:—** | | | | | | |
| Salary of Assistant Secretary | 290 | 0 | 0 | | | |
| Salary of Office Assistant | 31 | 3 | 6 | | | |
| Wages (Commissionaire, Housekeeper, and Charwoman) | 156 | 15 | 6 | | | |
| Coal and Lighting | 41 | 13 | 2 | | | |
| House Expenses and Repairs | 369 | 9 | 6 | | | |
| Tea Expenses | 29 | 14 | 0 | | | |
| Insurances | 11 | 9 | 3 | | | |
| Accountants' Charges | 21 | 0 | 0 | | | |
| Commission on Recovery of Income Tax | 1 | 16 | 8 | | | |
| Printing | 127 | 1 | 6 | | | |
| Stationery | 76 | 1 | 5 | | | |
| Postages | 103 | 2 | 11 | | | |
| Illuminated Address | 3 | 3 | 0 | | | |
| Miscellaneous Expenses | 25 | 7 | 1 | | | |
| | | | | 1287 | 17 | 6 |
| ,, Balance, being excess of Income over Expenditure, carried to Balance Sheet | | | | 176 | 1 | 7 |
| | | | | £8120 | 12 | 3 |

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved— JOHN M. THOMSON,
SAMUEL RIDEAL,
JAMES J. DOBBIE.

## BALANCE SHEET.—THE CHEMICAL SOCIETY, 31st December, 1912.

### *Liabilities.*

| | £ | s. | d. | £ | s. | d. |
|---|---|---|---|---|---|---|
| To Subscriptions received in advance ... ... ... ... ... | | | | 301 | 10 | 0 |
| ,, Sundry Creditors ... ... ... ... ... ... ... ... ... | | | | 1185 | 5 | 7 |
| ,, Research Fund :— | | | | | | |
| As per last Balance Sheet ... ... ... ... ... ... | 10496 | 9 | 1 | | | |
| *Less* Excess of Expenditure over Income for the year | 15 | 3 | 7 | | | |
| | | | | 10481 | 5 | 6 |
| ,, Chemical Society : Excess of Assets over Liabilities :— | | | | | | |
| As per last Balance Sheet... ... ... ... ... ... ... | 20393 | 7 | 9 | | | |
| *Add* Excess of Income over Expenditure for the year | 176 | 1 | 7 | | | |
| | | | | 20569 | 9 | 4 |
| | | | | £32537 | 10 | 5 |

### *Assets.*

| | £ | s. | d. | £ | s. | d. | £ | s. | d. |
|---|---|---|---|---|---|---|---|---|---|
| By Investments (value when acquired):— | | | | | | | | | |
| £6730 Metropolitan Consolidated 3½ per cent. Stock | | | | 7212 | 8 | 6 | | | |
| £1050 London and North Western Railway 3 per cent. Debenture Stock ... ... ... ... ... ... ... | | | | 839 | 12 | 0 | | | |
| £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock | | | | 1650 | 0 | 0 | | | |
| £1400 India 2½ per cent. Stock ... ... ... ... ... | | | | 1316 | 1 | 0 | | | |
| £2400 Bristol Corporation 2½ per cent. Debenture Stock | | | | 2070 | 2 | 0 | | | |
| £4341 Midland Railway 2½ per cent. Preference Stock | | | | 3572 | 2 | 5 | | | |
| £1200 Leeds Corporation 3 per cent. Stock ... ... | | | | 1148 | 1 | 0 | | | |
| £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53 | | | | 1460 | 13 | 6 | | | |
| £1200 North British Railway 3 per cent. Debenture-Stock ... ... ... ... ... ... ... ... ... ... | | | | 1033 | 11 | 0 | | | |
| £700 Canada 3½ per cent Stock, 1930/50 ... ... ... | | | | 704 | 8 | 6 | | | |
| | | | | | | | 21001 | 19 | 11 |
| (Estimated present value of Investments, £17997 8s. 5d.) | | | | | | | | | |
| ,, Sundry Debtors :— | | | | | | | | | |
| Advertising Account ... ... ... ... | 75 | 7 | 0 | | | | | | |
| *Less* Commission accrued ... ... ... ... | 5 | 8 | 5 | | | | | | |
| | | | | 69 | 18 | 7 | | | |
| Messrs. Gurney & Jackson .. ... ... ... ... ... | | | | 460 | 7 | 1 | | | |
| Telephone Deposit ... ... ... ... ... ... ... | | | | 1 | 0 | 0 | | | |
| | | | | | | | 531 | 5 | 8 |
| ,, Subscriptions in Arrear, £493. Estimated to realise .. | | | | | | | 350 | 0 | 0 |
| ,, Amount paid on account of International Association of Chemical Societies ... ... ... ... ... ... ... | | | | | | | 10 | 0 | 0 |
| ,, Insurance paid in advance ... ... ... ... ... ... .. | | | | | | | 46 | 5 | 7 |
| ,, Cash at Bank, Current Account ... ... ... ... ... ... | | | | 106 | 8 | 10 | | | |
| ,, Cash in hand ... ... ... ... ... ... ... ... ... .. | | | | 10 | 4 | 11 | | | |
| | | | | | | | 116 | 13 | 9 |
| ,, Research Fund :— | | | | | | | | | |
| Investments (value when acquired): | | | | | | | | | |
| £1000 North British Railway 4 per cent. No. 1 Preference Stock ... .. ... ... ... ... ... ... | | | | 1010 | 0 | 0 | | | |
| £4400 Metropolitan Consolidated 3½ per cent. Stock | | | | 4587 | 18 | 0 | | | |
| £1034 Great Western Railway 2½ per cent. Debenture Stock ... ... ... ... ... ... ... ... ... | | | | 1049 | 15 | 11 | | | |
| £1142 16s. New South Wales 3 per cent. Stock ... | | | | 1000 | 0 | 0 | | | |
| £1122 Metropolitan Water Board 3 per cent. "B" Stock ... ... ... ... ... ... ... ... ... ... | | | | 1002 | 16 | 9 | | | |
| £1365 Midland Railway 2½ per cent. Debenture Stock | | | | 1010 | 0 | 9 | | | |
| £806 Victoria 3 per cent. Stock ... ... ... ... ... | | | | 706 | 6 | 2 | | | |
| | | | | 10366 | 17 | 7 | | | |
| (Estimated present value of Research Fund Investments, £9481 17s. 10d.) | | | | | | | | | |
| ,, Cash at Bank... ... ... ... ... .. ... ... ... ... | | | | 114 | 7 | 11 | | | |
| | | | | | | | 10481 | 5 | 6 |
| | | | | | | | £32537 | 10 | 5 |

## RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1912.

### *Income.*

| | £ | s. | d. | £ | s. | d. |
|---|---|---|---|---|---|---|
| To Dividends on:— | | | | | | |
| £1000 North British Railway 4 per cent. No. 1 Preference Stock ... ... ... ... ... ... .. ... ... ... ... | 37 | 13 | 4 | | | |
| £4400 Metropolitan Consolidated 3½ per cent. Stock ... | 145 | 0 | 4 | | | |
| £1034 Great Western Railway 2½ per cent. Debenture Stock | 24 | 6 | 10 | | | |
| £[illegible]42 16s. New South Wales 3 per cent. Stock... ... ... | 32 | 5 | 10 | | | |
| £[illegible] 22 Metropolitan Water Board 3 per cent. "B" Stock | 31 | 14 | 0 | | | |
| £1365 Midland Railway 2½ per cent. Debenture Stock ... | 32 | 2 | 8 | | | |
| £806 Victoria 3 per cent. Stock ... ... ... ... ... ... | 22 | 15 | 4 | | | |
| | | | | 325 | 18 | 4 |
| ,, Repayments of Research Grants:— | | | | | | |
| J. F. Thorpe ... ... ... ... ... ... ... ... ... ... ... | 4 | 18 | 5 | | | |
| C. O. Bannister ... ... ... ... ... ... ... ... ... ... | 1 | 12 | 6 | | | |
| A. J. Evans ... ... ... ... ... ... ... ... ... ... ... | 1 | 16 | 6 | | | |
| C. Gilling ... ... ... ... ... ... ... ... ... ... ... | 1 | 0 | 7 | | | |
| C. H. Hampshire... ... ... ... ... ... ... ... ... ... | 1 | 10 | 0 | | | |
| F. B. Thole ... ... ... ... ... ... ... ... ... ... ... | | | 6 | | | |
| G. Barger ... ... ... ... ... ... ... ... ... ... ... | 4 | 16 | 8 | | | |
| A. Clayton ... ... ... ... ... ... ... ... ... ... ... | 2 | 5 | 1 | | | |
| W. M. Roberts ... ... ... ... ... ... ... ... ... ... | 6 | 13 | 6 | | | |
| | | | | 24 | 13 | 9 |
| ,, Income Tax Recovered ... ... ... ... ... ... ... .. | | | | 20 | 3 | 6 |
| ,, Balance, being Excess of Expenditure over Income carried to Balance Sheet ... ... ... ... ... ... ... | | | | 15 | 3 | 7 |
| | | | | £385 | 19 | 2 |

### *Expenditure.*

| | £ | s. | d. | | £ | s. | d. | £ | s. | d. |
|---|---|---|---|---|---|---|---|---|---|---|
| By Grants to— | | | | *Brought forward*— | 185 | 0 | 0 | | | |
| F. W. Atack ... ... | 15 | 0 | 0 | R. W. L. Clarke ... | 5 | 0 | 0 | | | |
| J. C. Cain ... ... | 10 | 0 | 0 | R. G. Fargher... ... | 8 | 0 | 0 | | | |
| J. B. Cohen ... ... | 5 | 0 | 0 | J. Ferns ... ... ... | 5 | 0 | 0 | | | |
| C. R. Crymble ... | 5 | 0 | 0 | N. Hall ... ... ... | 5 | 0 | 0 | | | |
| J. C. Duff ... ... | 5 | 0 | 0 | R. T. Hardman ... | 5 | 0 | 0 | | | |
| A. E. Dunstan ... | 10 | 0 | 0 | C. Hollins... ... ... | 5 | 0 | 0 | | | |
| J. B. Firth ... ... | 7 | 0 | 0 | E. Hope ... ... ... | 18 | 0 | 0 | | | |
| F. C. Garrett... ... | 10 | 0 | 0 | A. Hopwood ... ... | 8 | 0 | 0 | | | |
| W. N. Haworth ... | 12 | 0 | 0 | J. Kenner ... ... | 5 | 0 | 0 | | | |
| J. Kenner ... ... | 5 | 0 | 0 | F. R. Lankshear ... | 15 | 0 | 0 | | | |
| J. W. McBain ... | 10 | 0 | 0 | F. A. Mason ... ... | 5 | 0 | 0 | | | |
| J. Martin ... ... | 6 | 0 | 0 | P. May ... ... ... | 8 | 0 | 0 | | | |
| C. Smith... ... ... | 10 | 0 | 0 | R. W. Merriman ... | 8 | 0 | 0 | | | |
| S. Smith ... ... ... | 5 | 0 | 0 | J. E. Myers ... ... | 5 | 0 | 0 | | | |
| F. B. Thole ... ... | 5 | 0 | 0 | M. Nierenstein ... | 5 | 0 | 0 | | | |
| A. Wallace ... ... | 5 | 0 | 0 | W. R. Pratt ... ... | 10 | 0 | 0 | | | |
| C. R. Young ... ... | 10 | 0 | 0 | R. Robinson ... ... | 15 | 0 | 0 | | | |
| S. D. Adshead ... | 5 | 0 | 0 | H. Rogerson ... ... | 10 | 0 | 0 | | | |
| G. Barger ... ... | 5 | 0 | 0 | D. Segaller ... ... | 5 | 0 | 0 | | | |
| T. V. Barker ... ... | 15 | 0 | 0 | V. Steele ... ... ... | 6 | 0 | 0 | | | |
| E. de B. Barnett ... | 5 | 0 | 0 | T. R. Stopford ... | 5 | 0 | 0 | | | |
| G. Blackstock ... | 7 | 0 | 0 | F. B. Thole ... ... | 7 | 0 | 0 | | | |
| O. L. Brady ... ... | 5 | 0 | 0 | E. R. Thomas ... ... | 8 | 0 | 0 | | | |
| F. D. Chattaway ... | 8 | 0 | 0 | | | | | 361 | 0 | 0 |
| *Carried forward*— | £185 | 0 | 0 | | | | | | | |
| ,, Longstaff Medallist ... ... ... ... ... ... ... ... | | | | | | | | 20 | 0 | 0 |
| ,, Longstaff Medal ... ... ... ... ... ... ... ... ... | | | | | | | | 1 | 10 | 0 |
| ,, Advertisements ... ... ... ... ... ... ... ... ... | | | | | | | | 2 | 9 | 0 |
| ,, Commission on Recovery of Income Tax .. ... ... | | | | | | | | 1 | 0 | 2 |
| | | | | | | | | £385 | 19 | 2 |

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
*Chartered Accountant*,
23, QUEEN VICTORIA STREET,
E.C.

*3rd March*, 1913.

Approved—
JOHN M. THOMSON,
SAMUEL RIDEAL.
JAMES J. DOBBIE.

At the request of the Rev. W. G. Searle, Keeper of Coins at the Fitzwilliam Museum, Cambridge, the Council has presented to the Museum copies of the Longstaff Medal and Faraday Medal.

The number of books borrowed from the Library during the year was 1,825, as against 1,808 during the previous year; of these 491 were issued by post, as against 419 in the preceding year.

The additions to the Library comprise: 135 books, of which 70 were presented; 482 volumes of periodicals (representing 237 journals), and 76 pamphlets; as against 171 books, 438 volumes of periodicals (representing 237 journals), and 87 pamphlets last year.

The Library is indebted to Mr. J. A. Audley for a welcome gift of early journals.

The yearly increasing size of the Library will necessitate the consideration in the immediate future of the provision of adequate accommodation for its growth. In a statement of the Librarian appended to the President's Address in 1890, it was recorded that the Library then contained 9,884 volumes, made up of 3,082 volumes of systematic works, and 6,802 periodicals, with the addition of 1,450 pamphlets. At the present time it is estimated that the Library contains 21,256 volumes, of which 5,983 are systematic works, 15,273 volumes of periodicals, together with 3,500 pamphlets. It is thus seen that in twenty-two years the periodicals in the Library have increased in number of volumes by 124·5 per cent., the systematic works by 94 per cent., and the general total by 115 per cent.

It is estimated that shelf-room for 7,000 volumes will be required to accommodate the increase of volumes for the next ten years. At the close of 1913 there will at least be an additional 650 volumes to accommodate, whilst the empty shelving now at liberty will only contain some 250 volumes. Therefore, not only for the future, but also for the immediate present, additional Library accommodation is essential, and the Council has referred this question to the House and Library Committees.

Taking into account the occurrence of some items of exceptional expenditure, such as the decoration of the whole building and the ventilation of some of our rooms, it is satisfactory to find that, after meeting these expenses out of the income for the year, there is still an excess of income over expenditure of £176 1*s.* 7*d.* In 1913 the needs of the Library in the direction of providing accommodation for its continuous growth will necessarily entail considerable outlay, as pointed out above. For 1912 the income from all sources amounted to £8120 12*s.* 3*d.*, and the expenditure to £7944 10*s.* 8*d.*; for 1911 the corresponding amounts were £7735 11*s.* 6*d.* and £7499 3*s.* 10*d.* respectively. In other words, our income has increased by £385 0*s*. 9*d*., and our expenditure by £444 16*s*. 10*d*. The redecoration, improvements in ventilation, etc., alone account for £265 of this, and the increase in cost of the *Journal* for £124 2*s*. 8*d*.

As it was found impossible without either realising some of our investments or raising the annual subscription to give to Fellows without charge Vol. V. of the Collective Index, the price charged for it (thirty shillings) was fixed so as to cover as nearly as possible the cost of printing and distribution. The cost of preparing the index for the press is included in the editor's salary, and under the new arrangements its publication has been arranged for with an expedition hitherto impossible. From the number of Fellows who have applied and the number of copies which we may reasonably hope to sell to the public through our publishers, it seems probable that this volume of the Collective Index will not entail any serious outlay on the part of the Society.

The net income of the Research Fund for the year amounted to £367 6*s*. 5*d*., and by drawing on the balance in hand to the extent of £15 3*s*. 7*d*., grants were made amounting in all to £361, whilst the Longstaff Medal and Honorarium accounted for the remaining £21 10*s*.

A Vote of Thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year, proposed by Mr. W. F. Reid, seconded by Mr. A. Chaston Chapman, was acknowledged by Professor Arthur W. Crossley.

The President then delivered his address entitled "The Walden Inversion." Sir William Tilden proposed a Vote of Thanks to the President, coupled with the request that he would allow his address to be printed in the Transactions. The motion was seconded by Professor Harold B. Dixon, and acknowledged by the President.

The Report of the Scrutators was presented, and the President declared that the following had been elected as Officers and Council for the ensuing year:

*President:* William Henry Perkin, Sc.D., LL.D., F.R.S.

*Vice-Presidents who have filled the Office of President:* Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.;

Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, D.Sc., LL.D., F.R.S.; Hugo Müller, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; the Rt. Hon. Sir Henry Enfield Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., F.R.S.

*Vice-Presidents:* Herbert Brereton Baker, M.A., D.Sc., F.R.S.; George Thomas Beilby, LL.D., F.R.S.; Horace Tabberer Brown, LL.D., F.R.S.; Edmund James Mills, D.Sc., LL.D., F.R.S.; Gilbert Thomas Morgan, D.Sc.; William Jackson Pope, M.A., F.R.S.

*Treasurer:* Alexander Scott, M.A., D.Sc., F.R.S.

*Secretaries:* Samuel Smiles, D.Sc.; James Charles Philip, M.A., D.Sc., Ph.D.

*Foreign Secretary:* Arthur William Crossley, D.Sc., Ph.D., F.R.S.

*Ordinary Members of Council:* George Barger, M.A., D.Sc.; Edward John Bevan; William Robert Bousfield, M.A., K.C.; Adrian John Brown, M.Sc., F.R.S.; Harold Govett Colman, D.Sc., Ph.D.; Frederick George Donnan, M.A., Ph.D., F.R.S.; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Martin Lowry, D.Sc.; Hugh Marshall, D.Sc., F.R.S.; Kennedy Joseph Previté Orton, M.A., Ph.D.; Sir Boverton Redwood, Bart., D.Sc.; Edward John Russell, D.Sc.

# PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 14th, 1913.

By PERCY FARADAY FRANKLAND, Ph.D., LL.D., ScD., F.R.S.

## *The Walden Inversion.*

IN the Pasteur Memorial Lecture which I had the honour to deliver in this room sixteen years ago, I made the following statement:

"Before leaving the subject of malic acid, it is worthy of note that it is in connection with this acid that undoubtedly one of the most important discoveries relating to optically active bodies has been made since the time of Pasteur; I refer to the remarkable transformation of lævomalic acid into dextromalic acid, and *vice versâ,* through the medium of the corresponding chlorosuccinic acids, which has been accomplished by Walden (*Ber.*, 1896, **29**, 133).

*l*-Malic acid ⟶ *d*-chlorosuccinic acid ⟶ *d*-malic acid.

*l*-Malic acid ⟵ *l*-chlorosuccinic acid ⟵ *d*-malic acid."

It is with regard to this phenomenon, now so well known under the name of *Walden Inversion,* that I propose to offer some remarks to-day.

The past sixteen years have shown that the importance which I then attributed to Walden's discovery was fully justified, for this phenomenon is attracting more and more attention both from the experimental and the speculative sides.

Sir Oliver Lodge, in the fascinating lecture which he recently delivered to us on the discovery of radioactivity, made the very pertinent remark that:

"A discovery of real and essential novelty can never be made by following up a train of prediction. It is often made during the process of following a clue, but the clue does not logically lead to it. . . . The discovery which has been pointed to by theory is always one of profound interest and importance, but it is usually the close and crown of a long and fruitful period; whereas the discovery which comes as a puzzle and a surprise usually marks a fresh epoch and opens a new chapter in science."

Walden's discovery was certainly a puzzle and a surprise, for it did not fit into any pre-existing theory of optical activity, and had not been anticipated as a corollary to van't Hoff's theorem of the asymmetric carbon atom. It is highly probable that it may mark an epoch in our views with regard to the mechanism of the process of substitution in general.

As is well known, the Walden inversion has so far only been observed in the case of the substitution of a group directly attached to the asymmetric carbon atom itself in one or other of the following transformations:

$$\mathrm{R_1R_2R_3\textcircled{C}{-}OH}\;\begin{array}{l}\nearrow\ \mathrm{R_1R_2R_3\textcircled{C}{-}Cl}\\ \searrow\ \mathrm{R_1R_2R_3\textcircled{C}{-}Br}\end{array}$$

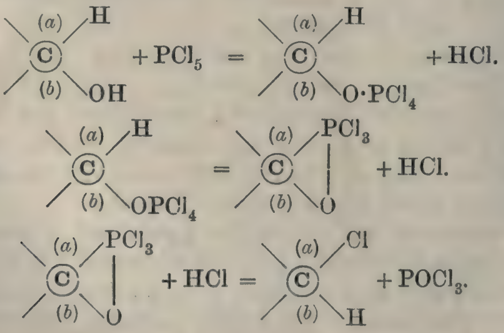
$$\mathrm{R_1R_2R_3\textcircled{C}{-}Cl(Br}\;\begin{array}{l}\nearrow\ \mathrm{R_1R_2R_3\textcircled{C}{-}OH}\\ \searrow\ \mathrm{R_1R_2R_3\textcircled{C}{-}NH_2}\end{array}$$

$$\mathrm{R_1R_2R_3\textcircled{C}{-}NH_2}\;\begin{array}{l}\nearrow\ \mathrm{R_1R_2R_3\textcircled{C}{-}OH}\\ \searrow\ \mathrm{R_1R_2R_3\textcircled{C}{-}Cl(Br)}\end{array}$$

Prior to the discovery of the Walden inversion, it would have been assumed that in such a substitution the entering group would either take the place of the extruded group, in which case the configuration would remain unaltered, or that it should take up any other position *without preference*, in which case there would be formed 50 per cent. of the one enantiomorph and 50 per cent. of the other, with the result that the product would be inactive (racemisation).

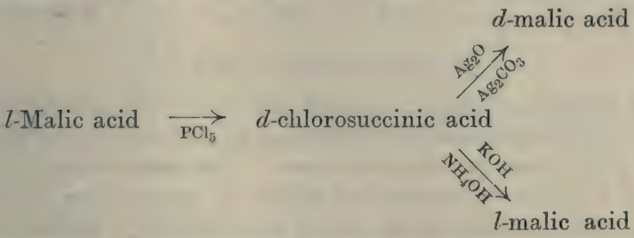
The discovery of the Walden inversion showed that in some of these substitutions there may be a *preferential* assumption of the position formerly occupied by one of the other groups, $R_1$, $R_2$, or $R_3$, attached to the asymmetric carbon atom, resulting therefore in a preponderating, or, indeed, in some cases the almost exclusive, production of the enantiomorphous configuration (inversion).

Prof. Armstrong, with his characteristic resource, was the first to furnish a tentative theoretical explanation of this unexpected phenomenon (T., 1896, **69**, 1399). He suggested the formation of two intermediate compounds, thus:



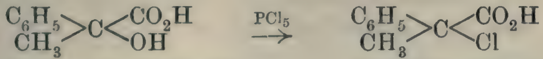
The merit of this ingenious explanation depends on its accounting for the preservation of the asymmetry of the carbon atom throughout the change without importing any new conceptions of combination or of valency.

It would, however, be difficult to apply this explanation to the optical inversions, which Walden soon discovered must take place when some bases hydroxylate a halogen acid. Thus, inasmuch as silver oxide and potassium hydroxide transform one and the same chlorosuccinic acid into the two enantiomorphous malic acids respectively, it follows as a necessary consequence that in one or other of these transformations an inversion must occur. Thus:



From the above, it is obvious that irrespectively of whether or not a configurative change occurs in the transformation of *l*-malic acid into *d*-chlorosuccinic acid, in one or other of the transformations of the latter into *d*-malic and *l*-malic acid respectively an inversion must occur (Walden and Lutz, *Ber.*, 1897, **30**, 2795; Walden, *Ber.*, 1897, **30**, 3146).

It is again obvious, also, that the above mechanism proposed by Armstrong could not be applied to the action of $PCl_5$ on an ·OH group attached to a tertiary carbon-atom. Thus:



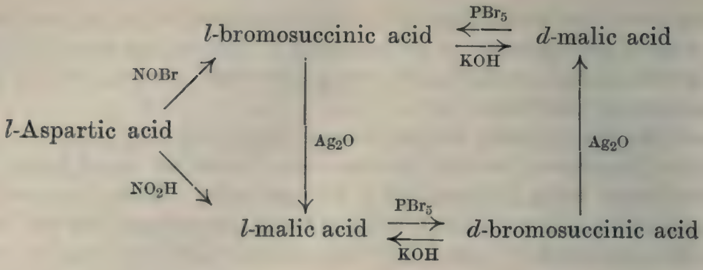
$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}CO_2H\\OH\end{matrix} \xrightarrow{PCl_5} \begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}CO_2H\\Cl\end{matrix}$$

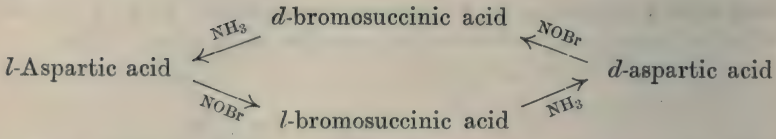
α-Hydroxy-α-phenylpropionic acid. *d*-α-Chloro-α-phenylpropionic acid.

but, of course, it might be argued that in this particular case no change of configuration does actually occur (McKenzie and Clough, T., 1910, **97**, 1016, 2564; 1912, **101**, 390).

The great importance of this phenomenon of optical inversion has not only led to much speculation, but fortunately also to a large amount of experimental work, for which we are indebted to Walden, Lutz, Purdie, and more especially to Emil Fischer and to McKenzie.

In a number of cases the complete cycle of changes from a given optically active compound to its enantiomorph and back again to the original compound has been realised. Thus, a single example will illustrate the beautiful symmetry of the results obtained:





This example, however, equally illustrates the difficulties with which we are confronted in attempting an explanation, for at which of the steps does the inversion occur? The fundamental difficulty is that we have at present no means of ascertaining whether a change of sign in any of the above steps betrays a change of configuration, and, conversely, we are equally ignorant as to whether identity of sign in the case of two different compounds corresponds with identity of configuration. Thus, in passing from *l*-aspartic to *d*-aspartic acid, we know that an inversion has taken place, but we do not know whether the change of configuration has occurred in passing from *l*-aspartic acid to *l*-bromosuccinic acid, or in passing from the latter to *d*-aspartic acid. Some speculations have assumed the one, and some the other hypothesis.

It is usual and convenient to designate replacement without change of configuration as *normal*, and with change of configuration, *abnormal*, and this convention will be adopted throughout the present address.

Much discussion has taken place as to which of the replacements in question are to be regarded as normal and which as abnormal, but the most painstaking examination of the data has so far failed to detect any convincing evidence bearing on the subject. I would, however, draw attention to some of the more striking regularities which appear to emerge from an examination of the known facts.

### I.—*Action of* $PCl_5$ *and* $PBr_5$ *on Hydroxy-compounds.*

In practically all well-established cases, the treatment of an active hydroxy-acid with phosphorus pentachloride (or bromide) results in the production of a chloro-acid (bromo-acid), with change of sign. A similar change of sign has also been found in most cases to accompany the action of phosphorus pentachloride on the esters of such hydroxy-acids, as far as these have been investigated.

A similar change of sign has recently been observed by McKenzie (*Brit. Assoc. Reports*, 1912; this vol., p. 687) to occur when $PCl_3$ acts on phenylmethylcarbinol with formation of phenylmethylchloromethane. This case is of particular interest, as it furnishes the first example of a Walden inversion occurring in connexion with a compound not containing either a free or esterified carboxyl group in the molecule. In the following table I have summarised the results obtained with $PCl_5$:

*Action of* $PCl_5$ *and* $PBr_5$ *on Hydroxy-compounds.*

| | | |
|---|---|---|
| l-*Malic acid*<br>l-*Malic esters* | $\xrightarrow{\mathrm{PCl_5}}$ | d-*Chlorosuccinic acid.* |
| (d)-*Lactic acid*<br>(Supposed to be really of lævo-configuration, because it forms lævorotatory salts and esters) | $\xrightarrow[\mathrm{PBr_5}]{\mathrm{PCl_5}}$ | d-*Chloropropionic acid.*<br>d-*Bromopropionic acid.* |
| l-β-*Hydroxybutyric* Me-*ester*<br>(Acid and ester have same sign) | $\xrightarrow{\mathrm{PCl_5}}$ | d-β-*Chlorobutyric* Me-*ester.* |
| l-β-*Hydroxybutyric acid*<br>(Acid and salts, lævo) | $\xrightarrow{\mathrm{PCl_5}}$ | d-β-*Chlorobutyric acid.* |
| l-*Phenylglycollic acid*<br>(Mandelic acid)<br>l-*Phenylglycollic* Et-*ester* | $\xrightarrow[\mathrm{PBr_5}]{\mathrm{PCl_5}}$ | d-*Phenylchloroacetic acid.*<br>d-*Phenylbromoacetic acid.* |
| * d-α-*Hydroxy*-β-*phenylpropionic acid* | $\xrightarrow{\mathrm{PCl_5}}$ | (l-α-*Chloro*-β-*phenylpropionic acid.*) |
| l-α-*Hydroxy*-β-*phenylpropionic* Et-*ester* | $\xrightarrow{\mathrm{PCl_5}}$ | l-α-*Chloro*-β-*phenylpropionic ester.* |
| l-α-*Hydroxy*-α-*phenylpropionic acid*<br>(Atrolactinic acid) | $\xrightarrow{\mathrm{PCl_5}}$ | d-α-*Chloro*-α-*phenylpropionic acid.* |
| l-α-*Hydroxy*-α-*phenylpropionic* Et-*ester.* | $\xrightarrow{\mathrm{PCl_5}}$ | d-α-*Chloro*-α-*phenylpropionic* Et-*ester.* |
| l-β-*Hydroxy*-β-*phenylpropionic acid.*<br>(Similarly with the *d*-acid) | $\xrightarrow[\mathrm{PBr_5\ or\ PCl_5}]{\mathrm{HBr\ or}}$ | d-β-*Bromo*-β-*phenylpropionic acid.* |
| d-*Phenylmethylcarbinol* | $\xrightarrow{\mathrm{PCl_3}}$ | -*Phenylmethylchloromethane.* |

* McKenzie and Barrow (T., 1911, **99**, 1914) find that no change of sign takes place in the case of the action of $PCl_5$ on the Et-ester, but they assume that a change takes place in the action on the free acid. The free *d*-hydroxy-acid gives with $PCl_5$ a dextrorotatory chloro-acid chloride, which they believe to be the chloride of the *l*-chloro-acid (see also p. 735).

*Note.*—The following anomalous results have been recorded by Guye and Jordan (*Bull. Soc. chim.*, 1896, [iii], **15**, 495), in which $PCl_5$ and $PBr_5$ appear to act differently, thus:

$$\begin{tikzcd}
 & \begin{array}{c}CH_3\cdot CH_2\cdot CHCl\cdot CO_2Bu\,\mathit{iso}\\ {[\alpha]_D}\ -10{\cdot}5^\circ.\end{array} \\
\begin{array}{c}CH_3\cdot CH_2\cdot CH(OH)\cdot CO_2Bu\,\mathit{iso}\\ {[\alpha]_D}\ -7{\cdot}7^\circ.\end{array} \arrow[ur, "PCl_5"] \arrow[dr, "PBr_5"'] & \\
 & \begin{array}{c}CH_3\cdot CH_2\cdot CHBr\cdot CO_2Bu\,\mathit{iso}\\ {[\alpha]_D}\ +6{\cdot}7^\circ.\end{array}
\end{tikzcd}$$

The great uniformity with which the action of $PCl_5$ is attended by a change of sign naturally suggests that the use of this reagent causes an inversion of the configuration. A very slight acquaintance, however, with the changes of sign which may accompany substitutions more remote from the asymmetric carbon atom at once shows that any such sweeping conclusion would be quite unjustifiable. Thus:

| | | |
|---|---|---|
| *l*-Amyl alcohol<br>(lævorotatory) | → | *l*-amyl acetate<br>(dextrorotatory) |
| *d*-ethyl tartrate<br>(dextrorotatory) | → | *d*-ethyl dibenzoyltartrate<br>(lævorotatory) |

are two of a very large number of examples which might be cited.

Very striking and instructive evidence as to the difficulty of connecting change of sign with change of configuration is furnished by experiments which I made in conjunction with Dr. Andrew Turnbull some thirteen years ago, but of which the results have not yet been published. We investigated the action of $PCl_5$ on the lævorotatory ethereal salts of glyceric acid, and obtained the corresponding esters of $\alpha\beta$-dichloropropionic acid, exhibiting the following optical relations:

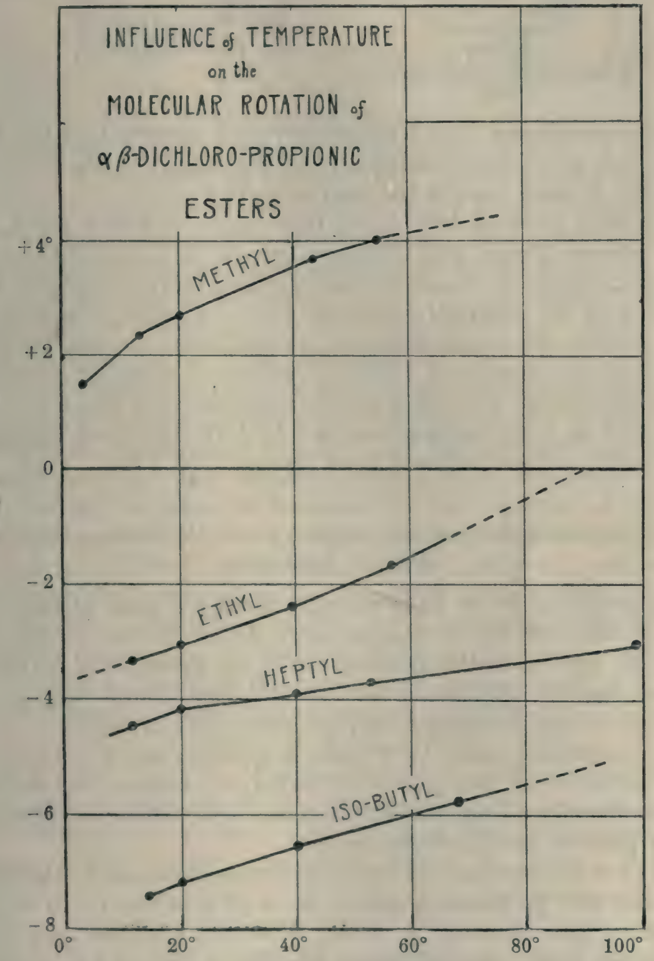
| | $[M]_D^{15^\circ}$. | | | $[M]_D^{20^\circ}$. |
|---|---|---|---|---|
| Methyl glycerate ..... | −5·76° | → | Methyl $\alpha\beta$-dichloropropionate...... | +2·67° |
| Ethyl ,, ...... | −12·30 | → | Ethyl ,, ...... | −3·06 |
| *iso*Butyl ,, ...... | −23·05 | → | *iso*Butyl ,, ...... | −7·20 |
| Heptyl ,, ...... | −23·05 | → | Heptyl ,, ...... | −4·17 |

From the above it might be argued that in the case of the methyl ester $PCl_5$ had acted abnormally (change of configuration), whilst in that of the higher homologous esters the action was normal (configuration unchanged). This argument is, however, at once seen to be untenable by a study of the influence of temperature on the rotation of the $\alpha\beta$-dichloropropionates.

From the diagram it will be seen that whilst rise of temperature increases the dextrorotation of the methyl ester, it diminishes the lævorotation of the higher esters, whilst if the latter were of enantiomorphous configuration to the methyl ester, their lævorotation would doubtless be increased by rise of temperature.

### II.—*Action of Thionyl Chloride on Hydroxy-compounds.*

The relations between the active hydroxy-compounds and their chloro-derivatives can again be investigated by using thionyl chloride as the chlorinating agent. The following transformations are known to occur:



*With Change of Sign.*

| | | |
|---|---|---|
| l-*Malic acid*<br>l-*Malic esters* | $\xrightarrow{SOCl_2}$ | d-*chlorosuccinic acid.* |
| l-α-*Hydroxy*-β-*phenylpropionic* Et-*ester.* | $\xrightarrow{SOCl_2}$ | d-α-*chloro*-β-*phenylpropionic* Et-*ester.* |
| d-*Ethyl tartrate** | $\xrightarrow{SOCl_2}$ | l-*ethyl dichlorosuccinate.* |

* P. Frankland and Lea, unpublished.

### Without Change of Sign.

*Phenylmethylcarbinol*
*Phenylglycollic acid* (Mandelic acid)
*Phenylglycollic* Et-*ester*
*β-Hydroxy-β-phenylpropionic acid*

l-*α-Hydroxy-α-phenylpropionic acid.* (Atrolactinic acid.)
l-*α-Hydroxy-α-phenylpropionic* Et-*ester.*

Thus the existing data are quite sufficient to show that the action of $SOCl_2$ is much more variable, from the point of view of effecting a change of sign, than is the case with $PCl_5$.

*It is very striking that in all those cases in which* $SOCl_2$ *leads to no change of sign, and therefore, as may be assumed for present purposes, also to no change of configuration, there is a phenyl group attached to the asymmetric carbon atom. Indeed, it will be seen later that the direct attachment of phenyl to the asymmetric carbon atom leads to exceptional behaviour in several different connexions.*

The phenomena attending the reactions brought about by $HNO_2$ and NOCl on amino-compounds, and by $NH_3$ and bases on halogen compounds, will be discussed later (see pp. 728, 730).

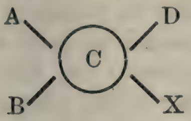
### Recent Speculations with regard to the Mechanism of the Walden Inversion.

The proposals which have recently attracted most attention are those of Emil Fischer on the one hand, and of Werner on the other, and both depend on the importation of the principle of attractions exerted by the asymmetric carbon atom on groups not actually attached by the ordinary four valencies of the carbon.

The process suggested by Fischer is perhaps best appreciated by a consideration of the concrete illustrative example, the action of liquid ammonia on monobromopropionic acid, which he pictures as taking place in the following manner.

One or more molecules of ammonia become attached to the bromopropionic acid by residual affinity so as to give rise to an additive product ("*polymolecule*"). Then, when the bromine separates in the ionised form, the $NH_2$-group can either take the place of the latter, in which case there will result no change of configuration, or one of the other three groups takes the place vacated by the bromine, and the $NH_2$ takes the place vacated by that group, with the result that inversion will have occurred (E. Fischer, *Annalen*, 1911, **381**, 132).

Werner (*Ber.*, 1911, **44**, 881), on the other hand, takes the asymmetric carbon atom with its four different groups, A, B, D, X, as forming the tetrahedron, in which X is the group that suffers replacement. This tetrahedron will have four faces: (1) ABX,



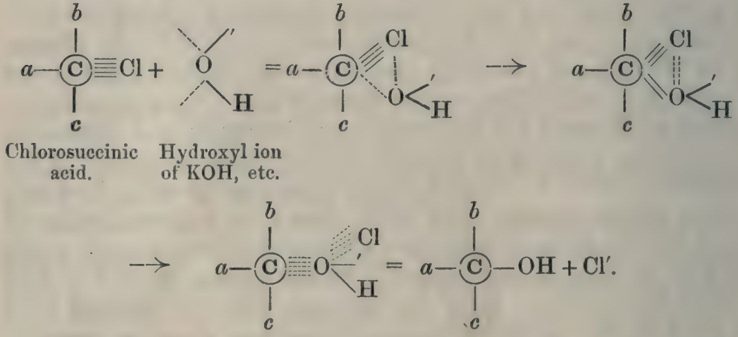
(2) ADX, (3) BDX, and (4) ABD, towards each of which the central carbon atom may be supposed to be capable of attracting an external group. If such an external group capable of replacing X be attracted to any one of the three faces, (1), (2), or (3), contiguous to X, then the replacement will take place without configurative change; on the other hand, if the group is attracted to the plane (4), diametrically opposite to X, then replacement will result in the production of the enantiomorphous configuration.

This mechanism is extremely simple in its conception, and Werner's mode of expression perfectly clear and definite. It postulates that by the mere attraction of the external group to any of the three faces (1), (2), and (3), the original configuration is already guaranteed before the removal of X, whilst if the attraction be to the face (4), then the opposite configuration is similarly ensured. The mechanism involves no reference to one group taking the place of another, for as a matter of fact the entering group will not in the first instance, nor doubtless even in the condition of final equilibrium, take up the exact position previously occupied by any other group present in the original molecule. It is only the configuration, which in three cases will be the same, and in the fourth case the opposite of the original configuration.

It appears to me that the mechanisms suggested by E. Fischer and by Werner are essentially the same, the differences being, for the most part, only differences of terminology. There is, however, a special merit about the Werner picture, inasmuch as it emphasises an important property of the tetrahedral model representing the asymmetric carbon, to which I do not think that attention had been hitherto called, namely, that with regard to a given group X attached to the carbon atom there are *four* positions towards which a fifth group can become attracted by the carbon atom, and that of these four positions three are identical, and one different from the point of view of the configuration resulting when the group X is eliminated.

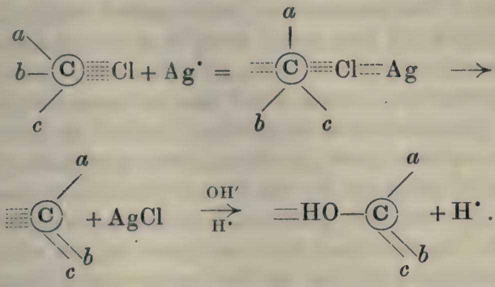
The more general terms in which the Fischer mechanism is formulated appear to me, however, to have one advantage. Fischer distinctly says that it is by no means necessary that the attracted group (for example, $NH_3$) should be attached to the carbon atom (*Annalen*, 1911, **381**, 132), but that *it may be attached to one of the four substituents* (*Annalen*, 1912, **394**, 352), the essential being that it should belong to the molecule. I think that this reservation is of importance, and likely to commend itself to chemists, as it is just in the case of a saturated atom of carbon (as the asymmetric carbon atom must of necessity be) that we have least right to postulate its possession of residual affinity. It is, moreover, highly significant that the groups attached to the asymmetric carbon which suffer replacement in the reactions with which we are concerned are precisely of such a kind (halogens, hydroxyl, $NH_2$) that we can safely predicate their possession of residual affinity in a high degree. It would appear therefore much more reasonable to suppose that the reagent is attracted by the residual affinity of a group which is known to possess it than by the residual affinity of the saturated atom of carbon, which very possibly does not possess any. The bearing of this on the phenomena of substitution in general is sufficiently obvious.

Yet another mechanism depending on the idea of residual valency has been proposed by J. Gadamer (*Chem. Zeit.*, 1910, **34**, 1004; 1912, **36**, 1327). Gadamer emphasises the necessity for assuming the formation of intermediate compounds in order to preserve continuous asymmetry during the process of substitution, and he illustrates the possibility of substitution occurring with and without change of configuration by the case of chlorosuccinic acid, in which the action of a *cation* (for example, silver) is supposed to lead to change of configuration, whilst the action of an *anion* (for example, hydroxyl) is attended with no change of configuration. Thus:



(N.B.—The divisibility of valency is indicated by a sheaf of dotted lines. The tendency of oxygen to become quadrivalent is also indicated by dotted lines.)

Thus the substitution of Cl by OH in the above scheme takes place without change of configuration. On the other hand, when the silver salt of chlorosuccinic acid is heated with water, the substitution of Cl by OH takes place according to the following scheme, in which the attack of the silver ion on the chlorine is the primary cause of the reaction:



In this process the chlorine is gradually withdrawn from the sphere of attraction of the carbon by the silver cation, and the other three groups (*a*, *b*, *c*), tending to set themselves in a plane with the carbon atom, leave the region opposite to the chlorine vacant for the attachment of the anion OH′, the substitution being thus accomplished with change of configuration.

In my opinion, the mechanism suggested by Gadamer in the case of the anion is really the same as that of Fischer and more especially of Werner, inasmuch as it is merely an elaboration of the idea that the ·OH, if attracted to one or other of the three planes adjacent to the Cl, necessitates replacement without change of configuration. On the other hand, Gadamer's scheme for the change of configuration resulting from the action of the cation appears to me to possess some elements of novelty, although it is in no way excluded by, or inconsistent with, the schemes of E. Fischer and Werner.

A most ingenious model illustrating this mode of effecting a change of configuration has been devised by my pupil and collaborator, Mr. Garner, who developed the idea quite independently of Gadamer.

This model, as well as the one described by Garner (P., 1912, **28**, 65) a year ago, appear to me to be by far the best yet devised for illustrating some of the remarkable properties of the asymmetric carbon atom.

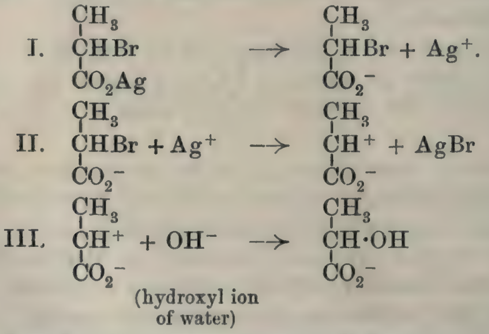
A very interesting consideration is raised by Gadamer, who points out that the preservation of optical activity in the substitution of a group attached to an asymmetric carbon atom is inconsistent with the old idea of one group replacing another, for that would involve a momentary attachment of only three groups, which would immediately lead to the production of a symmetric system (the three groups falling into one plane with the carbon atom), and by addition of a new group to this system racemisation should occur.

Gadamer, however, does not definitely discard the old idea of substitution, but accounts for the preservation of the activity by assuming that if the asymmetry is preserved without change of configuration, then the new group must have become attached before the three groups have swung into one plane with the carbon atom, and if the asymmetry is preserved with change of configuration, then the new group must have become attached at a moment when the three groups have through their momentum swung beyond the position in which they are in one plane with the carbon atom.

It appears to me much preferable to avoid this highly fanciful picture, and to assume that in a substitution the entering group becomes potentially attached to the carbon atom (either on one of the three planes adjacent to or on the plane diametrically opposite to the extruded group) *before the extruded group is actually detached.* This much simpler conception makes the fact of the retention of optical activity when substitution takes places at an asymmetric carbon atom serve as a demonstration of the truth of the idea which has so long been favoured by many chemists that addition of some kind must invariably precede substitution.

These considerations also lead up to the very interesting question of whether optical activity can be preserved in the case of an asymmetric system becoming ionised at the central atom.

That the ionisation of a group attached to an asymmetric carbon atom does not in general arise depends on the circumstance that an atom of carbon attached to four different groups cannot be the essential part of an electrolyte; but in the case of the halogen fatty acids some ionisation of the halogen atom, and therefore of the residual group, is often considered probable; thus Biilmann (*Annalen*, 1911, **388**, 338) supposes the transformation of silver α-bromopropionate into α-hydroxypropionate in aqueous solution to take place in the following manner:



$$\text{I.}\quad \begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CO_2Ag \end{array} \longrightarrow \begin{array}{l} CH_3 \\ | \\ CHBr + Ag^+ . \\ | \\ CO_2^- \end{array}$$

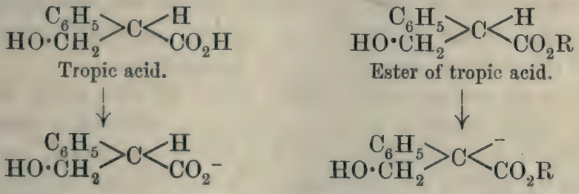
$$\text{II.}\quad \begin{array}{l} CH_3 \\ | \\ CHBr + Ag^+ \\ | \\ CO_2^- \end{array} \longrightarrow \begin{array}{l} CH_3 \\ | \\ CH^+ + AgBr \\ | \\ CO_2^- \end{array}$$

$$\text{III.}\quad \begin{array}{l} CH_3 \\ | \\ CH^+ + OH^- \\ | \\ CO_2^- \end{array} \longrightarrow \begin{array}{l} CH_3 \\ | \\ CH{\cdot}OH \\ | \\ CO_2^- \end{array}$$

(hydroxyl ion of water)

Inasmuch as the activity is preserved in the above transformation, it follows that these reactions involve the preservation of asymmetry in the amphoteric ion figured in II and III. I imagine that some chemists would condemn the above explanation of the reaction on the ground that the supposed ionisation would lead to inactivity. In the classical investigations of Pope and Peachey and of Smiles on the optically active derivatives of sulphur, selenium, and tin, many of the compounds had their rotatory power determined in the ionised state, with the asymmetric atom involved in the ionisation.* There is therefore abundant evidence that a tetravalent asymmetric atom can retain its asymmetry in the ionised condition. There is, however, also very striking evidence that the asymmetry in such cases is very unstable, and, indeed, the racemisation phenomena exhibited by the optically active tin compounds described by Pope and Peachey (P., 1900, **16**, 42, 116) are extremely remarkable, and quite unlike anything encountered in the case of the optically active compounds of carbon.

It has been suggested that evidence of ionisation at an asymmetric atom being a cause of racemisation is furnished by the different behaviour of tropic acid and its esters in respect of racemisation by OH-ions. Thus, Gadamer and Kuntze have found (*Chem. Zeit.*, 1910, **34**, 1004) that whilst the esters of tropic acid are readily racemised, the acid itself is not racemised by OH-ions. Gadamer attributes this difference to the acid being ionised at the $CO_2H$ group, whilst the ester, which is a pseudo-acid, only becomes ionised in the presence of OH-ions, thus:



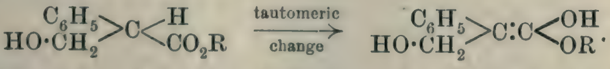
$$\begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}H\\CO_2H\end{matrix} \qquad \begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}H\\CO_2R\end{matrix}$$

Tropic acid. Ester of tropic acid.

$$\downarrow \qquad\qquad \downarrow$$

$$\begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}H\\CO_2^-\end{matrix} \qquad \begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}-\\CO_2R\end{matrix}$$

It would, however, appear probable that the ionisation of the ester should be preceded by tautomeric change, which would alone destroy the asymmetry, thus:



$$\begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}H\\CO_2R\end{matrix} \xrightarrow[\text{change}]{\text{tautomeric}} \begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C{:}C<\!\begin{matrix}OH\\OR\end{matrix}.$$

That an ionised quadrivalent atom should be capable of preserving its asymmetry is not so surprising, if ionisation be regarded as resulting from the combination of the electrolyte with the maximum number of water molecules which it can hold by means of the residual valency of the oxygen (P. Frankland, *Nature*, 1904, **70**, 222). Nor is it surprising that these comparatively loosely bound water molecules (which are doubtless not permanently attached but continually undergoing alternate dissociation from and reunion with the ion) should cause the asymmetry to be of a more ephemeral character than when they are replaced by a univalent group permanently attached in the ordinary way. Indeed, their alternate dissociation from and reunion with the ion will possibly give opportunity to a series of changes in configuration (Walden inversion), which will sooner or later lead to the complete racemisation of the ion. In fact, the above conception of ionisation as being caused by union of the electrolyte with water indicates that electrolytic dissociation and reassociation must be regarded as essentially processes of substitution, and, if these processes take place at an asymmetric atom, opportunities will be afforded for their being attended by configurative change.

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* Pope and Harvey (T., 1901, **79**, 831) and Jones (T., 1904, **85**, 229) have also found very rapid autoracemisation in the case of optically active ammonium iodides, but, as this takes place in non-ionising solvents, they attribute the change to decomposition of the ammonium salt into tertiary amine and alkyl iodide followed by recombination.

There is thus a remarkable agreement between the several more plausible explanations which have been suggested with regard to the mechanism whereby the Walden inversion may occur, but unfortunately all the attempts which have hitherto been made to apply these explanations to specific cases have proved singularly unfruitful.

Thus, Walden originally suggested that the action of $PCl_5$ was normal, and that in the hydroxylation of the resulting chloro-compound the action of KOH was also normal, but that of AgOH abnormal (that is, caused change of configuration).

Biilmann (*Annalen*, 1911, **388**, 335), on the other hand, has indicated what appears to be an intrinsic difference between the hydroxylation of a halogen acid by means of KOH, on the one hand, and by AgOH on the other. In the former case the process is dependent on the action of OH-ions, and in the latter to Ag-ions. The difference is attributed to the difference between the potassium and the silver salts of the halogen acid. The hydroxylation of the potassium salt is usually very slow, whilst that of the silver salt is generally very rapid, depending, as it is supposed to do, on the attack of the silver ion on the halogen with formation of insoluble, and therefore undissociated, silver haloid. That the undoubted occasional difference between the configuration of the hydroxy-acid obtained, according as KOH or AgOH is employed for the hydrolysis, may be connected with the soluble and ionised nature of the K-haloid, on the one hand, and the insoluble and non-ionised Ag-haloid on the other, is rendered the more probable, as Biilmann points out, inasmuch as HgO has been found to yield the same hydroxy-acid as AgOH, and the Hg-haloids, as is well known, are but very slightly ionised in solution.*

The great difference in the mode of hydrolysis of the alkaline and silver salts of halogen acids has also been established by the important investigations of Senter (T., 1907, **91**, 460; 1909, **95**, 1827; 1910, **97**, 346; 1911, **99**, 95, and later).

Gadamer, again, bases his speculations, as we have seen, on the action of OH-ions in the case of KOH, and on that of Ag-ions in the case of AgOH; but this harmony between Biilmann and Gadamer is only superficial, for whilst Biilmann draws the inference that the Ag-ions probably lead to hydrolysis without change of configuration, Gadamer comes to precisely the opposite conclusion.

Another endeavour is made by Biilmann to connect the supposed mechanism of the Walden inversion with specific instances of the phenomenon. Owing to the rapid and straightforward action of nitrous acid on amino-acids, he assumes that the transformation:

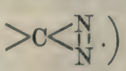
$$\text{amino-acid} \xrightarrow{HNO_2} \text{hydroxy-acid}$$

occurs without change of configuration. I would suggest that this hypothesis is favoured by the consideration that both the aspartic and the malic acid which occur in the vegetable kingdom are likely to have the same configuration, and that, as a matter of fact, the natural malic acid is the one which is produced by the action of nitrous acid on natural aspartic acid.

By analogy, also, he assumes that NOCl and NOBr react on amino-acids without change of configuration:

$$\text{amino-acid} \xrightarrow[NOBr]{NOCl} \frac{\text{chloro-acid}}{\text{bromo-acid}}.$$

On the other hand, Biilmann thinks that in the action of NOCl and NOBr on the esters of amino-acids, a configurative change may occur because, in the action of nitrous acid on aminoacetic ester, diazoacetic ester is actually formed, thus indicating that the diazo-group can, in the case of the ester of the amino-acid, actually come into connexion with the asymmetric carbon atom itself. (If the diazo-ester were actually formed, of course, complete racemisation should occur, because in the diazo-ester the asymmetry is lost, thus:



$$>C<\begin{matrix}N\\ \|\\ N\end{matrix}.)$$

Then, if it be assumed that in the case of NOCl or NOBr the halogen attaches itself to the carbon atom where the diazo-group would do so, we should have:

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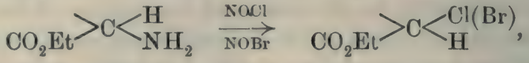
* Of great importance in this connexion are the investigations of Walden (*Ber.*, 1899, **32**, 1833) on the action of a whole series of bases on the halogen-succinic acids, and by McKenzie and Clough (T., 1909, **95**, 779) on the action of a similar series of bases on phenylchloroacetic acid.



$$\mathrm{CO_2Et}{>}\mathrm{C}{<}{\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{NH_2}}} \xrightarrow[\text{NOBr}]{\text{NOCl}} \mathrm{CO_2Et}{>}\mathrm{C}{<}{\genfrac{}{}{0pt}{}{\mathrm{Cl(Br)}}{\mathrm{H}}},$$

and the transformation would be accompanied by change of configuration.

This is in very plausible harmony with the observed differences between the action of NOBr on several amino-acids and their esters respectively, thus:

*Comparative Action of* NOCl, NOBr, *and* $HNO_2$ *on Free Amino-acids and their Esters.*

I. *d*-Alanine (HCl-salt, dextrorotatory) $\xrightarrow{\text{NOBr}}$ *l*-bromopropionic acid.
$\xrightarrow[\text{HNO}_2]{}$ *d*-lactic acid (zinc salt and esters lævorotatory).
*d*-Alanine ester $\xrightarrow{\text{NOBr}}$ *d*-bromopropionic ester.

(E. Fischer and O. Warburg, *Annalen*, 1905, **340**, 171; *Ber.*, 1906, **39**, 2895; 1907, **40**, 489.)

II. *l*-Leucine (HCl-salt, dextrorotatory) $\xrightarrow{\text{NOBr}}$ *l*-α-bromo*iso*hexoic acid.
*l*-Leucine ester (pure ester, dextrorotatory) $\xrightarrow{\text{NOBr}}$ *d*-α-bromo*iso*hexoic ester.

(E. Fischer, *Ber.*, 1906, **39**, 2929; *Annalen*, 1907, **357**, 13; *Ber.*, 1901, **34**, 445; 1907, **40**, 502.)

III. *l*-Aspartic acid (natural) $\xrightarrow{\text{NOCl}}$ *l*-chlorosuccinic acid.
$\xrightarrow{\text{NOBr}}$ *l*-bromosuccinic acid.
$\xrightarrow[\text{HNO}_2]{}$ *l*-malic acid.
*l*-Aspartic ester $\xrightarrow{\text{NOBr}}$ *d*-bromosuccinic ester.

(Tilden and Marshall, T., 1895, **67**, 494; Walden, *Ber.*, 1895, **28**, 2768; E. Fischer, *Ber.*, 1901, **34**, 453; 1904, **37**, 4599; 1907, **40**, 489, 1053; 1908, **41**, 889, 2891; 1909, **42**, 1219; 1910, **43**, 2020; Lutz, *Ber.*, 1908, **41**, 841; *Zeitsch. physikal. Chem.*, 1909, **70**, 256.)

IV. *d*-Phenylalanine $\xrightarrow{\text{NOBr}}$ *d*-α-bromo-β-phenylpropionic acid
*l*-Phenylalanine ester $\xrightarrow{\text{NOBr}}$ *d*-α-bromo-β-phenylpropionic ester.

(E. Fischer and Schoeller, *Annalen*, 1907, **357**, 11.)

To the above may be added the following partial data:

V. *l*-Phenylglycine (HCl-salt, lævorotatory) $\xrightarrow{\text{NOBr}}$ *d*-phenylbromoacetic acid.
$\xrightarrow[\text{HNO}_2]{}$ *d*-mandelic acid.

(McKenzie and Clough, T., 1909, **95**, 777.)

VI. *d*-Glutamic acid $\xrightarrow{\text{NOCl}}$ *l*-α-chloroglutaric acid.
$\xrightarrow[\text{NO}_2\text{H}]{}$ *l*-α-hydroxyglutaric acid. (salts, lævorotatory.)

(E. Fischer and Moreschi, *Ber.*, 1912, **45**, 2447.)

VII. *d*-β-Aminobutyric acid $\xrightarrow{NOCl}$ *l*-β-chlorobutyric acid.
$\xrightarrow[NO_2H]{}$ *l*-β-hydroxybutyric acid.

(E. Fischer and Scheibler, *Annalen*, 1911, **383**, 337.)

VIII. *d*-α-Amino-α-phenylpropionic acid $\xrightarrow[+HCl]{HNO_2}$ *l*-α-chloro-α-phenylpropionic acid.
$\xrightarrow[HNO_2]{}$ complete racemisation.

(McKenzie and Clough, T., 1912, **101**, 391.)

IX. *d*-β-Amino-β-phenylpropionic acid $\xrightarrow{HNO_2}$ *l*-β-hydroxy-β-phenylpropionic acid.
(in alcohol, lævorotatory.)

(E. Fischer, Scheibler and Groh, *Ber.*, 1910, **43**, 2020.)

X. *l*-Valine (HCl-salt, lævorotatory) $\xrightarrow{NOBr}$ *d*-α-bromo*iso*valeric acid.
$\xrightarrow[HNO_2]{}$ *l*-α-hydroxy*iso*valeric acid.
(salts, dextrorotatory)

(E. Fischer and Scheibler, *Ber.*, 1908, **41**, 889, 2891.)

*Note.*—The following transformations recently obtained by Holmberg (*Ber.*, 1912, **45**, 1003) are of interest:

*d*-Phenylethylamine $\xrightarrow{HNO_2}$ *l*-phenylmethylcarbinol.
$\xrightarrow[NOBr]{}$ *d*-phenylethyl bromide.

*l*-Phenylmethylcarbinol $\xrightarrow{PBr_5}$ *d*-phenylethyl bromide.*
$\downarrow$ AgOH
*l*-phenylmethylcarbinol.*

* The rotations are given as somewhat uncertain. (See also Marckwald and Meth, *Ber.*, 1905, **38**, 801.)

*Thus in all the cases investigated, the action of* NOBr *on the free amino-acid yields a bromo-acid of opposite configuration to that which is obtained by means of the same reagent on the ester.*

The question now arises as to whether in the case of the esters the transformation is accompanied by configurative change, and without configurative change in the case of the free acids, as postulated by Biilmann, or vice versâ.

There would appear to be no available data by means of which this question can be answered decisively. For the present therefore we have only the remarkable empirical regularity which is consistent with Biilmann's hypothesis, but would, of course, be equally consistent with its opposite.

The Biilmann hypothesis is, however, not borne out by the action of nitrous acid on the following amino-acids and their esters:

I. d-*Phenylglycine* (HCl-salt, dextrorotatory) $\xrightarrow{NO_2H}$ l-*mandelic acid.*
d-*Phenylglycine* Et-*ester* $\xrightarrow{NO_2H}$ l-*mandelic* Et-*ester.*
d-*Phenylglycine amyl ester* $\xrightarrow{NO_2H}$ l-*mandelic amyl ester.*

(E. Fischer and Weichhold, *Ber.*, 1908, **41**, 1293.)

II. d-β-*Amino-β-phenylpropionic acid* (HCl-salt, lævorotatory) $\xrightarrow{NO_2H}$ l-β-*hydroxy-β-phenylpropionic acid.* (in alcohol, lævorotatory)
d-β-*Amino-β-phenylpropionic* Et-*ester* (liquid ester, dextrorotatory) $\xrightarrow[\text{\& NaOH}]{NO_2H}$ l-β-*hydroxy-β-phenylpropionic acid.* (in alcohol, lævorotatory)

(E. Fischer, Scheibler, and Groh, *Ber.*, 1910, **43**, 2020.)

Thus, in the case of both these acids, the action of nitrous acid is the same on the ester as on the free acid itself. These are, however, the only cases in which the action of nitrous acid on an amino-acid and its ester appear to have been investigated.

*In both of these acids the phenyl group is attached directly to the asymmetric carbon atom; these might, therefore, quite conceivably prove to be exceptional cases.*

### *Action of* NH$_3$ *on Halogen Acids and their Esters which have themselves been obtained from Amino-acids and Esters.*

I. *d*-Alanine (HCl-salt, dextrorotatory) $\xrightarrow{NOBr}$ *l*-bromopropionic acid $\xrightarrow{\text{liq. } NH_3}$ *l*-alanine. (HCl-salt, lævorotatory)

(E. Fischer and Warburg, *Annalen*, 1905, **340**, 171; *Ber.*, 1906, **39**, 2895.)

*d*-Alanine ester. $\xrightarrow{NOBr}$ *d*-bromopropionic ester $\xrightarrow{\text{liq. } NH_3}$ *d*-alanine.

(E. Fischer, *Ber.*, 1907, **40**, 489.)

If the action of NOBr on the acid is normal, then the action of NH$_3$ on the bromo-acid is *abnormal*, whilst if the action of NOBr on the ester is abnormal, then the action of NH$_3$ on the bromo-ester is *abnormal* also, and there would be a double inversion in the passage from *d*-alanine ester to *d*-alanine. Moreover, whether the action of the NH$_3$ is normal or abnormal, it is the same in the case of the bromo-acid and its ester.

II. *l*-Aspartic acid $\xrightarrow{NOBr}$ *l*-bromosuccinic acid $\xrightarrow{NH_3}$ *d*-aspartic acid.

(For references, see p. 728.)

In this case, if NH$_3$ acts normally, then inversion must have taken place in the action of NOBr, which is contrary to the Biilmann hypothesis, but if NH$_3$ again acts *abnormally* in this case, then both I and II are consistent with the Biilmann hypothesis.

III. *l*-Valine (HCl-salt, lævorotatory) $\xrightarrow{NOBr}$ *d*-α-bromo*iso*valeric acid $\xrightarrow{NH_3}$ *l*-valine.

(E. Fischer and Scheibler, *Ber.*, 1908, **41**, 889.)

*d*-α-bromo*iso*valeric ester $\xrightarrow{NH_3}$ *d*-valine.

*d*-α-bromo*iso*valeric glycine $\xrightarrow{NH_3}$ *d*-valine.

(E. Fischer and Scheibler., *Ber.*, 1908, **41**, 2891.)

Thus the action of $NH_3$ on the acid is the opposite of that on the ester and the glycine respectively. If the action of NOBr is normal, as it should be (Biilmann), then that of the $NH_3$ on the bromo-acid is *normal* also, and on the ester and glycine *abnormal*.

IV. *l*-Leucine (HCl-salt, dextrorotatory) $\xrightarrow{\text{NOBr}}$ *l*-bromo*iso*hexoic acid $\xrightarrow{NH_3}$ *d*-leucine. (HCl-salt, lævorotatory)

*l*-Leucine ester $\xrightarrow{\text{NOBr}}$ *d*-bromo*iso*hexoic ester $\xrightarrow{NH_3}$ *l*-leucine. (HCl-salt, dextrorotatory)

(E. Fischer and Carl, *Ber.*, 1906, **39**, 3998; E. Fischer, *Ber.*, 1906, **39**, 2929; E. Fischer and Schoeller, *Annalen*, **357**, 13; E. Fischer, *Ber.*, 1901, **34**, 445; 1907, **40**, 502.)

If the action of NOBr on the acid is normal, then *the action of* $NH_3$ *on the bromo-acid is abnormal*, whilst if the action of NOBr on the ester is abnormal, then *the action of* $NH_3$ *on the bromo-ester is abnormal also.*

*Thus, in the case of alanine, leucine, and aspartic acid, the phenomena are consistent with the Biilmann hypothesis, provided that the action of* $NH_3$ *is abnormal.*

*Valine, however, differs from alanine and leucine, inasmuch as* $NH_3$ *must be supposed to act normally on the free* α*-bromo*isovaleric *acid, or, if the action of* $NH_3$ *is abnormal, then the action of* NOBr *on valine is abnormal also,* so that one or other of the steps is exceptional.

V. *d*-Phenylalanine (dextrorotatory in aqueous solution) $\xrightarrow{\text{NOBr}}$ *d*-α-bromo-β-phenylpropionic acid.

$\downarrow NH_3$

*l*-phenylalanine.

(E. Fischer and Carl, *Ber*, 1906, **39**, 4002.)

*l*-Phenylalanine Et-ester (HCl-salt, lævorotatory) $\xrightarrow{\text{NOBr}}$ *d*-α-bromo-β-phenylpropionic Et-ester

$\downarrow NH_3$

has not been investigated.

(E. Fischer and Schoeller, *Annalen*, 1907, **357**, 11.)

Thus, if the action of NOBr on *d*-phenylalanine is normal, as it should be (Biilmann), then the *action of* $NH_3$ *is abnormal.*

VI. *d*-Phenylglycine (HCl-salt, dextrorotatory) $\xrightarrow{\text{NOCl}}$ *l*-phenylchloroacetic acid $\xrightarrow{NH_3}$ *d*-phenylglycine.

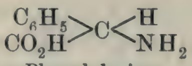
(McKenzie and Clough, T., 1909, **95**, 777.)

Thus, if the action of NOCl is normal, as it should be (Biilmann), then *the action of* $NH_3$ *is normal also.*

Thus, in the investigation of the behaviour of $NH_3$ on the halogen acids, basing the configuration of the latter on the Biilmann hypothesis with regard to the normality of the action of NOBr and NOCl on the free amino-acids, we find that the action of $NH_3$ is consistently abnormal, excepting in the case of the valine and phenylglycine series of transformations.

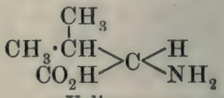
It will be seen later on (p. 734) that *l*-phenylchloroacetic acid (obtained from *d*-phenylglycine by the action of NOCl) forms an exception in its behaviour with KOH and $Ag_2O$ respectively. On the other hand, it does not form an exception, as regards its formation from *d*-mandelic acid by the action of phosphorus pentachloride, in which, as usual, the change of sign, and as is therefore assumed, the change of configuration, takes place. I think, however, that it may fairly be argued that phenylglycine and its derivatives (phenylchloroacetic acid and mandelic acid) all possess a very exceptional constitution (the phenyl and carboxyl groups being directly attached to the asymmetric carbon atom), and that, therefore, exceptional behaviour should occasion the less surprise.

The constitution of valine is perhaps also, in certain respects, not unlike that of phenylglycine:



$$\begin{matrix}C_6H_5\\CO_2H\end{matrix}>C<\begin{matrix}H\\NH_2\end{matrix}$$

Phenylglycine.



$$\begin{matrix}CH_3\cdot\overset{CH_3}{\overset{|}{C}}H\\CO_2H\end{matrix}>C<\begin{matrix}H\\NH_2\end{matrix}$$

Valine.

I may mention in this connexion that in all cases in which we have this same grouping of phenyl attached to the asymmetric carbon atom (irrespectively of whether this is in the α- or the β-position to the carboxyl group, if present), we have also a consistent behaviour of $SOCl_2$ on the hydroxyl compound (no change of sign) (see p. 720).

The assumptions made in the above reactions lead to the further conclusion that:

| | | | |
|---|---|---|---|
| d-*Alanine* (HCl-salt, dextrorotatory) | has the same configuration | as | l-*bromopropionic acid.* |
| l-*Leucine* (HCl-salt, dextrorotatory) | ,, | ,, | l-*α-bromoisohexoic acid.* |
| l-*Aspartic acid* (HCl-salt, dextrorotatory) | ,, | ,, | l-*chlorosuccinic acid.* |
| l-*Valine* (HCl-salt, lævorotatory) | ,, | ,, | d-*α-bromoisovaleric acid.* |
| d-*Phenylalanine* | ,, | ,, | d-*α-bromo-β-phenylpropionic acid.* |
| d-*α-Amino-α-phenylpropionic acid* | ,, | ,, | l-*α-chloro-α-phenylpropionic acid.* |
| d-*Glutamic acid* | ,, | ,, | l-*α-chloroglutaric acid.* |
| d-*β-Aminobutyric acid* | ,, | ,, | l-*β-chlorobutyric acid.* |
| d-*Phenylglycine* | ,, | ,, | l-*phenylchloroacetic acid.* |

Further, *if we assume the normal action of nitrous acid*, then:

| | | | |
|---|---|---|---|
| d-*Alanine*<br>(HCl-salt, dextrorotatory) | has the same configuration as | | d-*lactic acid*<br>(lævorotatory salts and esters). |
| d-*Serine*<br>(HCl-salt, lævorotatory) | ,, | ,, | l-*glyceric acid*<br>(dextrorotatory salts and esters). |
| l-*Aspartic acid*<br>(HCl-salt, dextrorotatory) | ,, | ,, | l-*malic acid*<br>(lævorotatory salts and esters). |
| l-*Valine*<br>(HCl-salt, lævorotatory) | ,, | ,, | l-*hydroxyisovaleric acid*<br>(dextrorotatory salts). |
| d-*Phenylglycine*<br>(HCl-salt, dextrorotatory) | ,, | ,, | l-*mandelic acid*. |
| d-β-*Aminobutyric acid* | ,, | ,, | l-β-*hydroxybutyric acid*. |
| l-β-*Amino-β-phenylpropionic acid*<br>(HCl-salt, dextrorotatory) | ,, | ,, | d-β-*hydroxy-β-phenylpropionic acid*<br>(in alcohol, dextrorotatory). |
| d-*Glutamic acid* | ,, | ,, | l-α-*hydroxyglutaric acid*<br>(lævorotatory salts). |

*If we assume the above relationships between the configurations of the amino-acids and the halogen acids on the one hand, and between the amino-acids and the hydroxy-acids on the other, then we can draw the further conclusions that:*

| | | | | |
|---|---|---|---|---|
| I. | l-*Bromopropionic acid* | has the same configuration as | | d-*lactic acid*<br>(lævorotatory salts and esters). |
| II. | l-*Chlorosuccinic acid* | ,, | ,, | l-*malic acid*. |
| III. | d-α-*Bromoisovaleric acid* | ,, | ,, | l-α-*hydroxyisovaleric acid*<br>(dextrorotatory salts). |
| IV. | l-*Phenylchloroacetic acid* | ,, | ,, | l-*mandelic acid*. |
| V. | l-α-*Chloroglutaric acid* | ,, | ,, | l-α-*hydroxyglutaric acid*. |
| VI. | l-β-*Chlorobutyric acid* | ,, | ,, | l-β-*hydroxybutyric acid*<br>(lævorotatory ester). |

In the above pairs of acids, the identity of configuration is based on the assumption that the hydroxy-acid is formed from the amino-acid without change of configuration, and similarly that the formation of the halogen from the amino-acid proceeds without configurative change. Proceeding further, we can, with the aid of these assumptions, now test other configurative relationships. Thus, the different action of different bases, especially of alkalis and silver oxide respectively, can be investigated. Thus:

$$\begin{tikzcd} & \text{$d$-lactic acid (lævo-salts).} \\ \text{I. $d$-$\alpha$-Bromopropionic acid} \arrow[ur, "\text{KOH}"] \arrow[dr, "Ag_2CO_3"'] & \\ & \text{$l$-lactic acid (dextro-salts).} \end{tikzcd}$$

Normal $= Ag_2CO_3$; Abnormal $=$ KOH.

*Note.*—$Ag_2O$ acts oppositely on the bromo-acid and on its glycine.

$$\begin{tikzcd}[column sep=large] & d\text{-malic acid.} \\ \text{II.}\quad l\text{-Bromosuccinic acid} \arrow[ur, "\mathrm{KOH}"] \arrow[dr, "\mathrm{Ag_2O}"'] & \\ & l\text{-malic acid.} \end{tikzcd}$$

Normal = $Ag_2O$ ; abnormal = KOH.

$$\text{III.}\quad d\text{-}\alpha\text{-Bromo}isovaleric\ \text{acid} \xrightarrow[\mathrm{Ag_2O}]{\mathrm{KOH}} l\text{-}\alpha\text{-hydroxy}isovaleric\ \text{acid (dextro-salts).}$$

Normal = $Ag_2O$ and KOH.

*Note.*—$Ag_2O$ acts in same way on the bromo-acid and on its glycine.

$$\begin{tikzcd}[column sep=large] & l\text{-mandelic acid.} \\ \text{IV.}\quad l\text{-Phenylchloroacetic acid} \arrow[ur, "\mathrm{KOH}"] \arrow[dr, "\mathrm{Ag_2CO_3}"'] & \\ & d\text{-mandelic acid.} \end{tikzcd}$$

Normal = KOH ; Abnormal = $Ag_2CO_3$.

$$\text{V.}\quad l\text{-}\alpha\text{-Chloroglutaric acid} \xrightarrow[\mathrm{Ag_2O}\ (24\ \text{hrs. in cold})]{\substack{\mathrm{H_2O}\ (2\ \text{hrs. at } 100^\circ) \\ \mathrm{NaOH}\ (24\ \text{hrs. in cold})}} \begin{array}{c} d\text{-}\alpha\text{-hydroxyglutaric} \\ \text{acid.} \\ \text{(salts, dextrorotatory)} \end{array}$$

$$\text{Abnormal} = \begin{cases} \mathrm{H_2O} \\ \mathrm{NaOH} \\ \mathrm{Ag_2O} \end{cases}$$

(E. Fischer and Moreschi, *Ber.*, 1912, **45**, 2447.)

*Note.*—The quantity of $Ag_2O$ added (1·5 grams to 0·5 acid) was only just sufficient to form the Ag-salt, which is insoluble. Therefore no evidence that Ag-ions had acted at all; may have been due to action of water alone. The polarimetric figures show that with NaOH, the reaction was complete in five hours in the cold.

$$\text{VI.}\quad d\text{-}\beta\text{-Chlorobutyric acid} \xrightarrow[\mathrm{Ag_2O}\ (3\ \text{days at } 37^\circ)]{\mathrm{H_2O}\ (40\ \text{hrs. at } 100^\circ)} l\text{-}\beta\text{-hydroxybutyric acid.}$$

$$\text{Abnormal} = \begin{cases} \mathrm{H_2O} \\ \mathrm{Ag_2O}. \end{cases}$$

(Fischer and Scheibler, *Ber.*, 1909, **42**, 1219.)

*Note.*—Even with $H_2O$ and $Ag_2O$ there is much racemisation, whilst NaOH and even $Na_2CO_3$ cause complete racemisation. The Ag-salt is very insoluble; four times the calculated quantity of $Ag_2O$ was employed in the hydrolysis.

The following two cycles of changes may also be included here:

$$\begin{tikzcd}[column sep=large] & \begin{array}{c} l\text{-}\alpha\text{-Hydroxy-}\alpha\text{-phenylpropionic acid} \\ (l\text{-atrolactinic acid}) \end{array} \arrow[r, "\mathrm{SOCl_2}"] & \begin{array}{c} l\text{-}\alpha\text{-chloro-}\alpha\text{-phenylpropionic} \\ \text{acid.} \end{array} \arrow[d, "\mathrm{Ag_2O}"] \\ \text{VII.*} & \begin{array}{c} d\text{-}\alpha\text{-Chloro-}\alpha\text{-phenylpropionic} \\ \text{acid} \end{array} \arrow[u, "\mathrm{Ag_2O}"] & \begin{array}{c} d\text{-}\alpha\text{-hydroxy-}\alpha\text{-phenylpro-} \\ \text{pionic acid} \\ (d\text{-atrolactinic acid).} \end{array} \arrow[l, "\mathrm{SOCl_2}"] \end{tikzcd}$$

---

* In these cases, the relative configurations of the hydroxy and halogen compounds can only be fixed by the relation of their rotation signs.

The results in the case of α-hydroxy-α-phenylpropionic acid are particularly important, as the abnormal action of $Ag_2O$ cannot be attributed to the action of water (OH-ions) predominating over the action of Ag-ions, because McKenzie and Clough (T., 1910, **97**, 1017) have shown that, using water alone, complete racemisation occurs, and that it is only when $Ag_2O$ is used that any active product is obtained.

VIII.*

$$\begin{tikzcd}
\text{$d$-Phenylmethylcarbinol} \arrow[r, "\mathrm{SOCl_2}"] & \text{$d$-phenylmethylchloromethane.} \arrow[d, "\mathrm{Ag_2O}\\ \mathrm{NaOH}"] \\
\text{$l$-Phenylmethylchloromethane} \arrow[u, "\mathrm{Ag_2O}\\ \mathrm{NaOH}"] & \text{$l$-phenylmethylcarbinol.} \arrow[l, "\mathrm{SOCl_2}"']
\end{tikzcd}$$

(McKenzie and Clough, *Brit. Assoc. Reports,* 1912 ; this vol., p. 687.)

Inasmuch as in both these cases, VII and VIII, $SOCl_2$ presumably acts normally (see p. 720), the action of $Ag_2O$ *and* NaOH *alike must be abnormal.*

Again, the following cycle has been realised (McKenzie and Wren, T., 1910, **97**, 1356):

IX.*

$$\begin{tikzcd}
\text{$d$-α-Hydroxy-β-phenylpropionic acid} \arrow[r, "\mathrm{PCl_5}"] & \text{$l$-α-chloro-β-phenylpropionic acid} \arrow[d, "\mathrm{CaCO_3+water}\\ \mathrm{NaOH}\\ \mathrm{Ag_2O}\ \text{very slowly}"] \\
\text{$d$-α-Chloro-β-phenylpropionic acid} \arrow[u, "\mathrm{CaCO_3+water}\\ \mathrm{NaOH}\\ \mathrm{Ag_2O}"] & \text{$l$-α-hydroxy-β-phenylpropionic acid.} \arrow[l, "\mathrm{PCl_5}"']
\end{tikzcd}$$

Inasmuch as the $PCl_5$ may be assumed to act abnormally, *all the hydroxylating agents appear to act normally.*

The following reactions are very interesting, and require special interpretation. I have indicated by the symbol $\circlearrowleft$ where I assume an inversion takes place, thus:

$$\begin{tikzcd}
\text{$l$-α-Hydroxy-β-phenylpropionic acid} \arrow[r, "\mathrm{HCl+}", "\mathrm{EtOH}"'] & \text{$l$-α-hydroxy-β-phenylpropionic ester} \arrow[d, "\circlearrowleft\ \mathrm{PCl_5}"] \\
\text{$d$-α-Hydroxy-β-phenylpropionic acid} & \text{$l$-α-chloro-β-phenylpropionic ester} \arrow[l, "\mathrm{CaCO_3+}"', "\mathrm{aq.\ EtOH}"] \\
\text{$l$-α-Hydroxy-β-phenylpropionic acid} \arrow[r, "\circlearrowleft", "\mathrm{PCl_5}"'] & \text{$l$-α-chloro-β-phenylpropionyl chloride} \arrow[d, "\mathrm{EtOH}"] \\
\text{$d$-α-Hydroxy-β-phenylpropionic acid} & \text{$l$-α-chloro-β-phenylpropionic ester} \arrow[l, "\mathrm{CaCO_3+}"', "\mathrm{aq.\ EtOH}"] \\
\text{$l$-α-Hydroxy-β-phenylpropionic acid} \arrow[r, "\mathrm{HCl+}", "\mathrm{EtOH}"'] & \text{$l$-α-hydroxy-β-phenylpropionic ester} \arrow[d, "\mathrm{SOCl_2}"] \\
& \text{$d$-α-chloro-β-phenylpropionic ester} \arrow[ul, "\mathrm{CaCO_3+aq.\ EtOH}"]
\end{tikzcd}$$

---

* See footnote, p. 734.

Thus, in all these cases, again the $CaCO_3$ *acts normally.* This conclusion involves the α-chloro-β-phenylpropionic ester having the same configuration as the hydroxy-acid or ester of opposite sign, just in the same way as I have supposed that ethyl glycerate (lævorotation) has the opposite configuration to the lævorotatory ethyl dichloropropionate (compare p. 718).

Again, the following may be considered:

$$\text{X.* } l\text{-}\beta\text{-Hydroxy-}\beta\text{-phenylpropionic acid} \underset{\text{Ag}_2\text{O, water or Na}_2\text{CO}_3}{\overset{\text{HBr or PBr}_5}{\rightleftarrows}} d\text{-}\beta\text{-bromo-}\beta\text{-phenylpropionic acid}$$

(McKenzie and Humphries, T., 1910, **97**, 121.)

$$d\text{-}\beta\text{-Hydroxy-}\beta\text{-phenylpropionic acid} \underset{\text{water}}{\overset{\text{HCl or PCl}_5}{\rightleftarrows}} l\text{-}\beta\text{-chloro-}\beta\text{-phenylpropionic acid}$$

(McKenzie and Barrow, T., 1911, **99**, 1915.)

$$\begin{tikzcd}
d\text{-}\beta\text{-Hydroxy-}\beta\text{-phenylpropionic acid} \arrow[r, "\text{SOCl}_2"] & d\text{-}\beta\text{-chloro-}\beta\text{-phenylpropionic acid.} \arrow[d, "\text{Water}"] \\
l\text{-}\beta\text{-Chloro-}\beta\text{-phenylpropionic acid} \arrow[u, "\text{Water}"] & l\text{-}\beta\text{-hydroxy-}\beta\text{-phenylpropionic acid} \arrow[l, "\text{SOCl}_2"]
\end{tikzcd}$$

(McKenzie and Barrow, *loc. cit.*)

In these reactions, again, if $PCl_5$ and $SOCl_2$ be assumed to act abnormally and normally respectively, then the action of *the water and other reagents would be uniformly abnormal* (that is, causing a configurative change).

The whole of the hydrolysis results (10 cases) may be thus summarised:

*Sign Changes in Hydrolysis of Halogen Compounds.*

Change of sign = +. No change of sign = 0.

| | | KOH, etc. | $Ag_2O$. |
|---|---|---|---|
| I. | †‡Bromopropionic acid | + | 0 |
| II. | †‡Bromosuccinic acid | + | 0 |
| III. | †Bromo*iso*valeric acid | 0 | 0 |
| IV. | †‡Phenylchloroacetic acid | 0 | + |
| V. | †α-Chloroglutaric acid | + | + |
| VI. | †‡β-Chlorobutyric acid | + ($H_2O$) | + |
| VII. | ‡α-Chloro-α-phenylpropionic acid | ... | + |
| VIII. | ‡Phenylmethylchloromethane | + | + |
| IX. | ‡α-Chloro-β-phenylpropionic acid | 0 | 0 |
| X. | ‡β-Bromo-β-phenylpropionic acid | + | + |

* See footnote, p. 734.

† The configurative relationship between the hydroxy- and the halogen compound can be tentatively fixed by the Biilmann hypotheses with regard to the action of $HNO_2$ and NOCl(NOBr).

‡ The configurative relationship can be fixed by the tentative hypothesis with regard to the action of $PCl_5(PBr_5)$ on the hydroxy-compound.

In the first six of the above cases there are sufficient data to admit of the two Biilmann hypotheses being tested. These hypotheses are:

(1) $NO_2H$, NOCl, and NOBr act *normally* on the free amino-acids, and *abnormally* on their esters.

(2) When KOH and $Ag_2O$ act oppositely on a halogen acid, the $Ag_2O$ acts *normally*, and the KOH abnormally.

The two cases (I and II) above are entirely consistent with the Biilmann hypotheses. In case III, the hypotheses are verified as regards $Ag_2O$, but not as regards KOH. In case IV, the results are the reverse of those which the hypotheses predict. In case V the result confirms the Biilmann hypothesis as regards NaOH, but contradicts it as regards $Ag_2O$. There is, however, no evidence that in this case there was any Ag-ion present in the solution. In case VI it is also doubtful whether the Ag-ion was the active agent, as the Ag-salt is very insoluble, and the reaction was carried out in very dilute solution.

By means of the configurative relations given on p. 736, we can further test the action of $PCl_5$, $PBr_5$, and $SOCl_2$ on the hydroxy-acids. Thus:

| | | | |
|---|---|---|---|
| I. | d-*Lactic acid* (lævo-salts and esters) | $\xrightarrow[PBr_5]{PCl_5}$ | d-*chloro(bromo)propionic acid* (change of configuration). |
| II. | l-*Malic acid* | $\xrightarrow[SOCl_2]{PCl_5}$ | d-*chlorosuccinic acid* (change of configuration). |
| III. | No data available. | | |
| IV. | l-*Mandelic acid* | $\xrightarrow[PBr_5]{PCl_5}$ | d-*phenylchloroacetic acid*<br>d-*phenylbromoacetic acid*<br>(change of configuration) |
| | | $\xrightarrow[SOCl_2]{}$ | l-*phenylchloroacetic acid* (configuration unchanged). |
| V. | No data. | | |
| VI. | l-β-*Hydroxybutyric acid* | $\xrightarrow[PCl_5]{}$ | d-β-*chlorobutyric acid* (change of configuration). |

Thus, in all the four cases in which the data are available, the halogen compounds of phosphorus effect a change of sign, which, on the previous assumptions, betrays a change of configuration, whilst out of the two cases in which the data are available for $SOCl_2$, in one there is change, and in the other no change of sign or configuration. It is very significant that the case in which the $SOCl_2$ causes no sign change and, as is assumed, no change of configuration, is the only one in which phenyl is directly attached to the asymmetric carbon atom. A regularity in connexion with this structure has already been pointed out (see p. 732).

## *Summary.*

As already pointed out, it would appear that there does not exist at the present time any criterion whereby the relation between the configuration of an optically active compound and that of a derivative from it can be decisively ascertained. Until the discovery of the Walden inversion it was always tacitly assumed that an optically active compound and a derivative prepared from it had the same configuration, excepting in so far as the preparation might be attended with racemisation phenomena (this statement is intended to include such cases as the preparation of *d*-gluconic acid from *d*-mannonic acid). The phenomenon of the Walden inversion shows, however, that we cannot admit such an assumption prima facie in the case of any derivative obtained by the substitution of a group attached to an asymmetric carbon atom.

In the absence of any criterion for definitely ascertaining configurative relationship, we naturally have recourse to hypotheses, and seek for cumulative evidence for or against them. Such hypotheses are likely to be based on (*a*) *whether the passage from one compound to another is or is not accompanied by a change of sign in the rotation;* (*b*) *whether the reaction which leads from one compound to the other is on general grounds likely or unlikely to be attended by a change of configuration.*

The hypotheses which I have endeavoured to investigate are:

(1) That the change of sign which almost invariably accompanies the action of $PCl_5$ or $PBr_5$* is, in the absence of evidence to the contrary, to be regarded as betraying a change of configuration. However, Pickard and Kenyon (T., 1911, **99**, 45; *Ber.*, 1912, **45**, 1592), as well as McKenzie and Humphries (T., 1910, **97**, 121) and McKenzie and Barrow (T., 1911, **99**, 1923), have also uniformly found a change of sign to occur when the halogen compound is prepared by means of halogen acid from the hydroxy-compound, so that the mechanism does not apparently depend on the phosphorus.

(2) That in those cases in which $SOCl_2$ brings about a change of sign, there is also a change of configuration. And inasmuch as in all cases known in which $SOCl_2$ does not bring about a change of sign, there is the uniform circumstance of a phenyl group being directly attached to the asymmetric carbon atom, it would appear that it is possibly this circumstance which leads to an exceptional behaviour of $SOCl_2$ in those cases. That the phenomena attending substitution at an asymmetric carbon to which a phenyl group is

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* For exceptions, see pp. 717, 718.

directly attached are of an exceptional character is closely connected with the observations both of E. Fischer and of McKenzie, that this particular structure is especially liable to give rise to extensive racemisation during substitution.

(3) For reasons already indicated, Biilmann has assumed the probability of there being no configurative change when $NO_2H$, NOCl, or NOBr act on the free amino-acids, but that configurative change may take place when these reagents act on the esters of the amino-acids.

There does not appear to be any experimental evidence that $NO_2H$ acts oppositely on amino-acids and on their esters respectively; in the only two cases investigated, on the contrary, the action is the same on both.

On the other hand, in the only four cases in which the action of NOCl or NOBr has been investigated both on a free amino-acid and on its ester, the action on the two is opposite.

By means of these assumptions we may tentatively fix the configurative relations between a number of amino-acids and their hydroxy- and halogen derivatives respectively. Thus data are available for tentatively fixing this relation between 9 amino-acids and 9 halogen acids, and between 8 amino-acids and 8 hydroxy-acids respectively.

(4) Having fixed these configurative relations, I have proceeded to investigate from this basis the several reactions in which a halogen is replaced by the $NH_2$-group.

Data are available for the investigation of six cases of such substitution (see pp. 730, 731).

In four out of these six cases the action of $NH_3$ proves to be *abnormal*, that is, the substitution of halogen by $NH_2$ is attended with configurative change. The two other cases, which may be called exceptional, are those of:

$$d\text{-}\alpha\text{-Bromo}\textit{iso}\text{valeric acid} \xrightarrow{NH_3} l\text{-valine}$$

$$l\text{-Phenylchloroacetic acid} \xrightarrow{NH_3} d\text{-phenylglycine.}$$

We may therefore perhaps tentatively conclude that the usual course of the substitution of a halogen by $NH_2$ is *abnormal* (that is, attended by configurative change) on the assumptions made in this investigation.

(5) Again starting from the configurative relations referred to in paragraph (3), I have investigated the several reactions in which a halogen is replaced by the OH-group. These are the reactions which have given rise to the recent suggestive speculations of Gadamer and of Biilmann, as well as to the interesting investigations of Senter.

Data are available in ten cases, but in several the data are unfortunately somewhat fragmentary, and the necessarily different conditions under which the hydroxylation takes place militate against the utility of the results for purposes of comparison.

In three out of the ten cases a different product is obtained, according as the hydroxylation is effected with $Ag_2O$ or with KOH respectively, and in two* of these three cases $Ag_2O$ acts *normally* and KOH *abnormally*, in accordance with the Biilmann hypothesis, whilst in the third † case it is KOH which acts *normally* and $Ag_2O$ *abnormally*.

In two cases (α-bromo*iso*valeric and α-chloro-β-phenylpropionic acids), both $Ag_2O$ and KOH act *normally*, whilst again, in the five remaining ‡ cases, all the hydrolysing agents act *abnormally*, that is, produce a configurative change.

It is evident therefore that just in the replacement of halogen by hydroxyl there is apparently great irregularity, and hence most difficulty in harmonising the results with the demands made by the speculations of either Biilmann ($Ag_2O$ normal, KOH abnormal) or Gadamer ($Ag_2O$ abnormal, KOH normal) respectively.

It is obvious that there are many complicating factors in these transformations; for example, the insolubility of the silver salts and the consequent uncertainty of whether there is an effective concentration of Ag-ions present. In my previous presidential address (T., 1912, **101**, 683), I called attention to the contradictory results which had been obtained in the relative facility with which AgBr separates from silver bromofumarate and bromomaleate respectively according to the conditions of experiment, and it is probable that similar complicating factors come into play in the reactions under discussion now.

The complexity of the reactions in which the halogen of halogen acids is replaced by hydroxyl is strikingly brought out by the extended investigations of Senter, in which some most unexpected phenomena have been brought to light. It is therefore not surprising that the configurative relations connected with these reactions should at present be so obscure.

There is one regularity in the hydroxylation results which is perhaps worthy of attention, and that is that in the only three cases investigated of compounds having a phenyl group directly attached to the asymmetric carbon atom, the action of silver oxide is abnormal (that is, attended with configurative change) according to the configurative relations which I have deduced from the assumptions made.

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* Bromopropionic acid and bromosuccinic acid.

† Phenylchloroacetic acid.

‡ α-Chloroglutaric acid, β-chlorobutyric acid, α-chloro-α-phenylpropionic acid, phenylmethylchloromethane, and β-bromo-β-phenylpropionic acid.

I would suggest that several distinct processes of hydroxylation, according to the conditions employed, should be recognised:

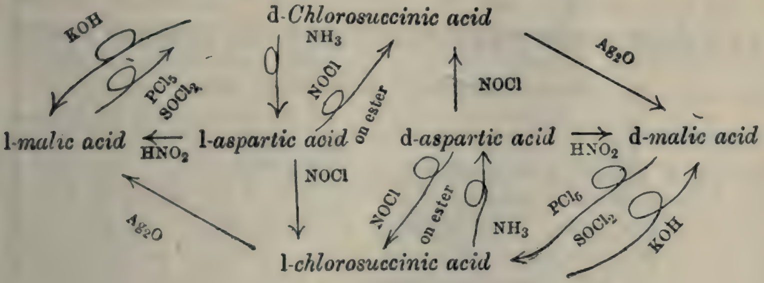
(1) The silver salt may in the first instance split off silver haloid *internally*, the hydroxyl ion of the water becoming simultaneously attached.

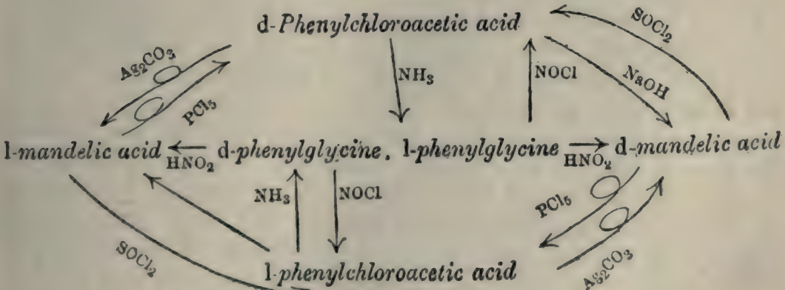
(2) The halogen may be removed by silver-ion, forming insoluble and non-ionised silver haloid, the hydroxyl-ion of the water becoming simultaneously attached.

(3) The halogen may be similarly removed by cations, forming soluble but non-ionised haloids (mercury, palladium, etc.).

(4) The halogen may become ionised and remain ionised in the form of halogen acid (when water acts alone) or as ionised haloids (when potash, soda, lime, etc., are used in the hydrolysis).

The following diagram, showing the transformations which have been effected in the case of malic and mandelic acids respectively, will perhaps best illustrate the configurative relations which have been developed in the present discussion. In this diagram the symbol ⟶ indicates a transformation *without*, and ⟲ a transformation *with configurative change.*





It must be clearly understood that the foregoing investigation, made of the available data, only displays the relative effects of the several reagents employed, and that these *relations* would be equally true if the terms *normal* and *abnormal* were employed in the opposite sense to that in which I have used them throughout, for we have at present, as I have so often reiterated, no criterion whereby the occurrence or non-occurrence of a configurative change in a process of substitution can be decisively tested.

It is evident that a very large amount of experimental work has still to be carried out before the numerous complex and highly important issues arising out of the phenomenon of the Walden inversion can be fully elucidated. I trust that the account which I have endeavoured to give of the present position of the subject may serve to indicate the various directions in which the inquiry can be advantageously prosecuted.

# OBITUARY NOTICES.

## PAUL ÉMILE (DIT FRANÇOIS) LECOQ DE BOISBAUDRAN.

Born 1838; Died May 28th, 1912.

**François Lecoq de Boisbaudran** belonged to the ancient Protestant nobility of Poitou and Angoumois; they were people of considerable fortune, which, however, the revocation of the Edict of Nantes caused to disappear. The property of Boisbaudran was sold; and his father Paul, together with his brother Scœvola, an old student of the École Polytechnique, started a wine business at Cognac. At first, the venture was not very successful; but as time went on things prospered, and young Lecoq entered the business, for it needed all the energy of the family to keep things going. Lecoq was blessed with an excellent mother; she was the daughter of an officer, and was exceptionally gifted; from her, her son learned the classics, history, and foreign languages. The writer made his acquaintance in the late '60's, when he visited Glasgow, "travelling in wine," and he spoke English fluently and with little accent, although he had not quite mastered the niceties of the language; on one occasion he astonished an elderly lady, his partner at dinner, by the remark, "Madam, the soup is devilish hot."

During the intervals of his travels he spent his small leisure in working through the courses of the École Polytechnique, of which he had procured the syllabus. He thus acquired a very general knowledge of science; but the problems of chemistry and physics were those which most attracted him; and he fitted up a modest laboratory, where he began to repeat the experiments and methods of analysis of which he had read in books. In this he was helped by the liberality of one of his uncles. It was in this laboratory that he made most of his early discoveries; it was there that gallium was first isolated. He met with encouragement from all members of his family. It was one in which old Protestant principles, fortified by persecution, survived; and its watchwords were justice, kindness, and the sense of personal responsibility; in such a family François Lecoq received his training.

De Boisbaudran's early work had reference to the phenomena of supersaturation of solutions. It was he who first showed that supersaturation is destroyed by contact with crystals of an isomorphous salt, and also that it is possible to prepare solutions of anhydrous salts in a supersaturated condition (1866 to 1869). Incidentally, he pointed out the presence of isodimorphism in double sulphates. In 1874 he published the interesting fact that octahedral faces are less readily soluble than cubical faces in the case of ammonium alum. In 1871 he was in advance of his time in suggesting devices for the electric deposition of metals for analytical purposes. His chief work, however, may be treated under three heads: (1) his spectroscopic studies; (2) their application to the discovery of gallium; (3) their application to his researches on the rare earths.

In 1865 Lecoq deposited a "pli cacheté" with the Academy of Sciences, which was opened by his request in 1871; he summarised its contents as follows: "It is well known that molecules the vibrations of which produce light have isochronous periods of oscillation, for they give rise to rays of determinate wave-length, constant for each substance. The force which tends to bring back the molecule to its centre of oscillation is the reaction of the ether on the molecule; this reaction remains constant so long as the mass and the velocity of the molecule do not change, but varies when the relative masses of the ether and the molecule vary. A heavier molecule therefore returns to its centre of equilibrium with less energy than a lighter, and consequently takes a longer time to oscillate through this point; its wave-length is greater. It is the vibration of the whole molecule which produces light; when a compound resists a high temperature without decomposing, its spectrum is different from that of its elements. In such a case, as in that of elements, the less refrangible rays are due to the heavier compound, when the compounds have the same chemical constitution." These ideas led him to the following conclusions:

"(1) The lines of a spectrum are derived from one or more primitive lines, which form an elementary group; this, by successive increases or diminutions of the wave-length, repeats itself in the spectrum without altering the general appearance.

"(2) For the same natural family, the mean wave-length of the elementary groups is a function of the respective atomic weights; the general form of the spectrum therefore persists on passing from one element of the same chemical type to another; the only change it undergoes is that due to the change of mass of the molecules.

"(3) In a series of analogous spectra, the mean wave-lengths of the harmonics are greater the higher the atomic or molecular weights of the elements or compounds which give the spectra."

In order to collect material for testing these generalisations, Lecoq made an elaborate study of the spectra of thirty-five elements, in some cases using the Bunsen burner to cause luminescence, in others an electric spark, and in others both. The results of these laborious investigations were published in 1874 in a handsome volume entitled "Spectres Lumineux." In observing spark spectra, he made use of a solution of a salt of the element to be examined, contained in a glass tube, through the bottom of which a platinum wire was sealed; this was made the negative pole; the positive was a stouter piece of platinum wire, a few millimetres above the surface of the liquid. In 1885, by reversing the current and making the liquid positive, he obtained phosphorescent bands instead of a line spectrum; by aid of this arrangement, he succeeded in discovering three new metals, to which he gave the provisional names $Z\alpha$, $Z\beta$, and $Z\gamma$; these have since been named dysprosium, terbium, and europium. He also produced phosphorescent spectra by directing the negative stream on to the substance in powder, placed in a vacuum; and, as early as 1866, he introduced the idea of solid solutions to chemistry. His view was that the spectrum is due to the dissolved substance, and he carried out many researches in reference to the subject. His conclusions differed, it may be remembered, from those of Sir William Crookes; an excellent summary of the controversy is to be found in the *Annales de Chimie et de Physique* for 1909, by M. Urbain.

Lecoq de Boisbaudran first attracted the universal attention of chemists by his discovery of gallium. In February, 1874, he began the investigation of 52 kilograms of blende from Pierrefitte (Hautes-Pyrenées). The solution of this mineral gave a deposit on metallic zinc which revealed in the spectroscope a hitherto unknown line of wave-length 4170; further research revealed another line of wave-length 4031. These two lines are not shown in the Bunsen flame, but they appear by aid of an oxy-hydrogen flame; Sir W. N. Hartley has recognised the wide distribution of gallium by their aid. In 1875 he had obtained several milligrams of gallium chloride; and he transferred his materials to Wurtz's laboratory in Paris, where he demonstrated the reality of his discovery. His experiments were recommenced with several hundred kilograms of blende, and in the same year he succeeded in preparing the metal by electrolysing a solution of the hydroxide in potassium hydroxide; he obtained more than a gram of metal. Later on, in collaboration with Jungfleisch, he obtained 75 grams of metal from over 4000 kilos. of blende. The extraction was carried out in the factory at Javel.

From his generalisation (2), already quoted on p. **744,** he calculated the atomic weight of gallium as 69·86; the mean of two sets of determinations gave the same figure. He also calculated the atomic weight from a periodic arrangement of the elements, which, although not published until 1895, was constantly discussed in the early '60's with Dumas and Friedel. It does not differ in any marked particular from those generally accepted.

One of the fruits of this magnificent work was the bestowal on him of the Cross of the "Legion d'Honneur"; he succeeded Malaguti as Correspondent of the Institute in 1878; he was awarded the Davy Medal in 1879; and the Prix Lacaze of 10,000 francs. He was elected a Foreign Member of our Society in 1888.

It was in 1869 that he began his work on rare earths; his familiarity with spectroscopic methods peculiarly fitted him for this task. In that year Lecoq showed that the didymium from cerite differed from that of samarskite; he had as a collaborator the American, Lawrence Smith. In July of that year he announced the discovery of samarium, defined by its absorption bands. Marignac separated the same element later, and characterised it by the letter Y. From Marignac, Lecoq obtained a specimen of earths separated during the fractionation which yielded samarium, and in it he detected a new element, subsequently named gadolinium. In 1904 he gave the provisional letter Z to the element contained in an earth separated from impure terbia, and this has been identified by Urbain as pure terbia.

In studying the spectra of solutions, in which the liquid was made the positive pole, Lecoq noticed a citron band as well as a green one in fractions of the rare earths precipitated by potassium sulphate. In 1886 he succeeded in obtaining the earth yielding the citron band in a pure state; and he named it dysprosium, a word meaning "difficult to obtain."

After 1895, family duties and failing health hindered his work. Along with M. le Comte de Gramont (to whose excellent article in the "Revue Scientifique" the writer is chiefly indebted for the facts of this notice), the spectrum of glucinum (beryllium) was studied; an account of his experiments was published in 1911. M. le Comte de Gramont is issuing a further volume on spectra, of which the work was carried out by Lecoq in his later years.

Lecoq de Boisbaudran married late in life, and his marriage brought him much happiness. His sufferings from anchylosis of the joints, which were very severe, were borne with stoical resignation. He passed away on May 28th, 1912, at the age of seventy-four.

W. Ramsay.

## EDWARD DIVERS.

Born November 27th, 1837; Died April 8th, 1912.

### I.

Edward Divers was born in London of Kentish ancestry November 27th, 1837. He had one brother, who was connected with the Thames Ironworks, and a sister. His sister, who survives him, is the widow of James O'Kinealy, a distinguished Colonial Judge, who had been a fellow student of Divers in Queen's College, Galway. In infancy Divers had an attack of inflammation of the eyes, which seriously impaired his vision, a defect which could not be remedied by glasses. Later in life, in 1884, an unfortunate explosion during an experiment so much aggravated this that he practically lost the use of his right eye. This defect of vision was a serious handicap to him throughout his life, and it is marvellous how notwithstanding he was able to conduct researches, as he did, involving the closest observational powers.

In 1850, at the age of thirteen, Divers entered the City of London School, one year after Perkin, where he came under the influence of one of the masters, Thomas Hall, who had been a student of Hofmann's at the Royal College of Chemistry, and who had become inspired by him as Divers himself and Perkin and so many others subsequently were. Hall gave experimental lectures in chemistry between class hours; there was no compulsion, no inducement, but simply the attraction of science and its boundless possibilities, both of its own advancement and of its applications to the welfare and happiness of mankind. By this natural and efficient process the fittest were attracted, and from Hall the way was opened to Hofmann and the Royal College for many who are now well known in the annals of science. We are indebted to Perkin and to Divers himself for an account of Hall and what he did for chemistry in such a quiet, unobtrusive manner (T., 1896, **69**, 599; Perkin Jubilee volume, 21).

This, the early years of the Royal College of Chemistry, is a period upon which chemists love to linger. The remarkable achievements going on around us to-day show that the boundaries of the unknown have not yet been reached, still there was a fruitfulness attending the work of the young Hofmann and his devoted followers, in Hanover Square, in Oxford Street, and in Jermyn Street, that arrests attention. Later, in the autumn of the life of that great leader, he told the writer that, at the time referred to, no matter what they touched, where they addressed their questionings to Nature, she seemed to respond willingly, disclosing important and suggestive results. With such a leader in research, with such a teacher, in the right meaning of the word, no wonder that those who came within his influence became inquirers and teachers too; and as he carried on the work of Liebig, so they carried on that of Hofmann. It was destined that Divers should carry it to Japan.

Divers was only one year at the College of Chemistry, the session 1852–3. This was the last session at the Oxford Street laboratories, the college being merged in the Jermyn Street School of Mines in 1853–4. Mr., now Sir William, Crookes was then assistant, and Divers ascribed much of the value of his training to the help which Mr. Crookes gave him. In 1853–4 Divers became a junior assistant in Stenhouse's laboratory in St. Bartholomew's Hospital Medical School, where Abel was then assistant, and both Kekulé and H. Buff were working. Stenhouse regarded Divers's defective vision too serious a hindrance to admit of the attainment of success in a chemistry career; but it is interesting to know that he was led afterwards to modify this opinion.

One of the effects of the movement associated with the arrival in this country of the Prince Consort, which gave rise to the Royal College of Chemistry, was the foundation in Ireland of the Queen's University, with its federated colleges in Belfast, Cork, and Galway. It was natural, therefore, that the chemistry chairs in those colleges should be intimately related to the College of Chemistry. Thus Blyth, Hofmann's assistant professor, was one of the first professors at Cork, and Rowney, an assistant of Hofmann's, became a professor at Galway, succeeding Liebig's student, Ronalds. Ronalds in 1854 required an assistant, and Divers accepted the position, and continued in the same capacity under Rowney, who became professor in 1856.

Divers went to Galway with the object of taking the University degree in medicine, one of the few scientific degrees then available, and at the same time to take advantage of the opportunities there afforded for teaching and research in chemistry. He remained there constantly until the completion of his medical curriculum, when he obtained the degree of M.D. in 1860, and afterwards, during the winter sessions until 1866, when he finally left Ireland and took up his abode in London, at Notting Hill. As assistant and demonstrator of chemistry in Galway for about twelve years, Divers was well known to the students, whom he attracted by his natural gifts as a teacher, and the late Prof. Allman, a well-known mathematician, often told the writer how he was himself attracted to Divers, and sought from him instruction in chemistry.

His medical experience was made use of in Galway as physician for a time to the fever hospital and in other minor appointments, and as a teacher of chemistry he was asked by the Committee of Council on Education to deliver popular lectures in Ballina and other places. After 1860, and until his Japanese appointment in 1873, he also held various teaching appointments in England, as Lecturer in Materia Medica at Queen's College, Birmingham, and, in London, as Lecturer in Medical Jurisprudence at Middlesex Hospital Medical School, and in Physics at Charing Cross Hospital Medical School. He was also Lecturer in Chemistry at the Albert Veterinary College, and contributed special reports from time to time to the medical journals on the quality of the London milk supply and other subjects.

Divers joined the Chemical Society in 1860, and in 1862 commenced the publication of the results of his experimental inquiries. His first paper is an account of a careful study of magnesium ammonium carbonate, which was followed in 1868 by one on zinc ammonium chloride, and in 1870 by three papers describing his classical investigation of the carbonates and carbamate of ammonium. He had studied in 1863 the spontaneous change which guncotton undergoes with formation of gelatinous acids, and then in 1871 appear two papers in which he begins the study of nitrites, and announces his discovery of hyponitrites, the study of which he afterwards made so much his own. Another very interesting subject was investigated in 1873 just before his Japanese appointment, the interaction of ammonia and ammonium nitrate. The work recorded in these papers is a fitting introduction to the more important results of his activity in Japan: it is characterised by accuracy even in the minutest detail and a keenness of observation all the more remarkable considering how much he was handicapped by his difficulty of sight.

In 1899, shortly after the death of his wife, Divers gave up his home in Japan and returned to this country. His interest in chemistry continued unabated, and especially in respect to those subjects upon which he had worked himself. But he will be remembered best as the centre of groups of younger workers, women as well as men, who looked to him as a leader, an old warrior, whom they delighted to honour. To them, particularly, he responded wholeheartedly, with a sympathy and affection they will not soon forget. His old University in Ireland, represented in 1897 by the Royal University, conferred on him its D.Sc. *honoris causa*, and the various societies in England and the British Association were glad to recognise his worth. He was President of Section B of the British Association (1902); Vice-President of the Chemical Society (1900–02); Vice-President of the Institute of Chemistry (1905), and the same year President of the Society of Chemical Industry. He was elected a Fellow of the Royal Society while in Japan, 1885.

A. S.

## II.

### *Dr. Divers's Life and Work in Japan.*

Dr. Divers came out to Japan in July, 1873. This country had then only begun to remodel its civilisation by systematically introducing Western sciences and institutions, and several seats of liberal and technical education, based on the Western systems, were being established in Tokyo. The Engineering College at Toranomon was one of these, and it was here that Dr. Divers was asked to teach General and Applied Chemistry, this institution being fortunate in obtaining, from the earliest period of its existence, the services of such able men of science as the late Prof. Ayrton, Profs. Milne and Perry, besides Dr. Divers. Dr. Henry Dyer, of Glasgow, was the Principal of the College, and, on his resignation in 1882, Dr. Divers was asked to occupy the post thus left vacant, besides holding the Professorship of Chemistry.

In 1886 the Engineering College was incorporated with the Tokyo University, in which the several departments of Law, Literature, Science, and Medicine had already been established, and from that time Dr. Divers's service was transferred to the College of Science of the newly reorganised Imperial University of Tokyo, where he held the Chair of Inorganic Chemistry until his return to England in 1899.

Coming out to Japan at the age of thirty-six and staying for twenty-six years, which were equally divided between the old Engineering College and the present College of Science, Divers spent the best part of his life in this country, and by his teaching and example during this long and meritorious service he greatly promoted the development of chemical science in Japan, besides contributing very largely to the general progress of chemistry.

It is true that during his first seven or eight years in Japan Divers did not publish anything, but this was only because his time was too much taken up with other matters to devote his attention to original work. Not only were his professorial duties very heavy during this period, but he was also being constantly asked by the Department of Public Works, to which the Engineering College at first belonged, to undertake the analysis of minerals, valuations of ores, assay of gold and silver, and so forth, besides being occasionally consulted on questions connected with the chemical industry of the country.

The first papers published by Divers after coming out to this country were, indeed, those bearing on Japanese minerals, and these were communicated to the meetings of the British Association held in York in 1881. In one of these papers he described his observations on the occurrence of selenium and tellurium in Japanese sulphur, and he subsequently obtained a quantity of these elements from the lead-chamber deposits of the Osaka sulphuric acid work. The material thus obtained enabled him, with the assistance of Shimosé, who greatly distinguished himself afterwards as the discoverer of a powerful explosive, to do some good work on these elements, among which reference may be made to the discovery of a new oxide of tellurium, of tellurium sulphoxide, and of a new and simple method for the quantitative separation of tellurium from selenium. These and other papers on tellurium and selenium were published in the *Journal of the Chemical Society* during the years 1883–1885.

Divers's activity as an investigator became suddenly and particularly prominent about this time, for although his energy never seemed to be appreciably diminished except for the last year or two of his residence in this country, he published no less than twenty-four papers within the two years 1884–1885 in the *Journal of the Chemical Society* alone, and with the exception of those on tellurium and selenium, together with two or three minor communications, all these papers and also others subsequently published by him refer to the chemistry of nitrogen and sulphur compounds, to which subject, indeed, few chemists have probably contributed more than he. It is quite impossible in this short notice to give anything like a brief summary even of the immense amount of work done by Dr. Divers in this particular field; only a few of the more important points brought to light by his work can therefore be offered for review.

Two years before coming out to Japan Dr. Divers published a very interesting and important paper on "The existence and Formation of Salts of Nitrous Oxide" (T., 1871, **24**, 484), and, taking up this work on hyponitrites again in 1884, he, in collaboration with Haga (T., 1884, **45**, 78), established the composition of silver hyponitrite to be $(AgNO)_x$ against the formula $Ag_4N_4O_5$ asserted to be true by Berthelot and Ogier. Several new modes of formation of hyponitrites were discovered at the same time, among which the ready decomposition of an oxyamidosulphonate by an excess of strong alkali into a hyponitrite and a sulphite (T., 1889, **55**, 760) according to the equation:

$$2KON(SO_3K)_2 + 4KOH = (KON)_2 + 2K_2SO_3 + 2H_2O,$$

is interesting as affording a proof that in hyponitrites the metallic radicle is not in direct union with nitrogen, but is united to it through oxygen. The reaction is also important as being suitable for preparing large quantities of hyponitrites, Kirschner's method of preparation being, in fact, based on this reaction.

In the paper entitled "On the constitution of some non-saturated oxygenous salts, and the reaction of phosphorus oxychloride with sulphites and nitrites" (T., 1885, **47**, 205), Divers brought forward strong reasons in favour of the sulphonic or unsymmetrical constitution of inorganic sulphites, and one of these was the very conclusive fact experimentally established by him that, by the action of phosphorus oxychloride on sodium sulphite, one-half of the sodium contained in the latter goes to form sodium chloride, whilst the other half is converted into sodium phosphate. Thus:

$$3SO_2(Na)(ONa) + POCl_3 = 3NaCl + (NaO)_3PO + 3SO_2.$$

At the same time, he showed that Carius's work, according to which thionyl chloride formed by the action of phosphorus pentachloride on inorganic sulphites was regarded as a direct product of the reaction and which formed the only experimental evidence in favour of the symmetrical constitution of the sulphites, had no significance whatever, inasmuch as thionyl chloride was doubtless produced by a secondary reaction between sulphur dioxide and phosphorus pentachloride. It was in the course of the work now under review, and, in fact, on November 24th, 1884, that Divers had a very serious accident, which cost him the loss of the sight of his right eye, it having been very badly cut by pieces of glass resulting from the sudden bursting of the bottle in which phosphorus oxychloride had been kept (compare *Chem. News*, 1885, **51**, 23).

In continuation of his work on the constitution of sulphites, Divers, in collaboration with Shimidzu, thoroughly investigated the very varied and numerous sulphites of mercury (T., 1886, **49**, 533), and brought to light many interesting peculiarities in the chemistry of this metal.

Fulminic acid and hydroxylamine also attracted a good deal of Divers's attention. Among other things, he and Kawakita proved, in a paper on "The constitution of the Fulminates" (T., 1884, **45**, 13), that formic acid formed a very important part of the products of decomposition of mercury fulminate by hydrochloric acid, a fact which had been quite overlooked by previous workers, who could not make out what the carbon of the fulminates became by this decomposition, whilst in the study of the formation of hydroxylamine from nitric acid (T., 1883, **43**, 443), it was shown that, of all the common metals, zinc or tin is best suited for effecting the reduction, and, further, in collaboration with Shimidzu (T., 1885, **47**, 597), that the presence of sulphuric or hydrochloric acid is essential for the production of large quantities of hydroxylamine, the non-addition of one of these acids yielding practically no hydroxylamine, but giving rise to the formation of ammonia and other products of reduction.

Of all subjects, however, the one which was most fully studied by Divers and which was made peculiarly his own was the chemistry of sulphonated nitrogen compounds. In collaboration with Haga, he showed that the numerous complex acids belonging to this group of compounds are the products of the reaction between sulphurous and nitrous acids, the base being essential only in so far as it protects the products of the reaction against hydrolysis, and that, contrary to the statements of previous workers, normal sulphites and nitrites have no action whatever on each other (T., 1900, **77**, 673). They further showed that the primary product of the reaction between sulphurous and nitrous acids is always hydroxylaminedisulphonic acid and nothing else, no derivative of dihydroxylamine or of any quinquevalent nitrogen being ever formed. All the substances supposed by others to be such were proved to be merely double salts of hydroxylaminedisulphonate and alkalinitrite, with or without alkali replacing the hydroxyl-hydrogen of the disulphonate, and to be synthetically obtainable from hydroxylaminedisulphonate, alkali nitrite, and alkali hydroxide

(T., 1900, **77**, 432). The chemistry of these rather complex compounds was thus considerably simplified.

Divers was pre-eminently an experimental chemist. He was always busily engaged in an experimental work of some sort, but rarely occupied with the theoretical study of chemical questions, and this aptitude of his mind is doubtless to be traced to the influence and teaching which he early received from A. W. Hofmann at the Royal College of Chemistry, and to which he often used to refer in his conversation. Divers, in his turn, also greatly encouraged the spirit of experimental research, and in this he was most successful, for besides those of his old pupils already named as his collaborators, who are also well known as independent investigators, several others have distinguished themselves by publishing important experimental work, of whom mention may be made of Dr. J. Takaminé, of New York, who prepared pure adrenaline for the first time, and Prof. M. Ogawa, of the Tohoku Imperial University, who discovered the new element nipponium. Reference may perhaps be made here to the work of Prof. M. Chikashigé, of the Kyoto Imperial University, who is also an old pupil of Divers, and who, according to his suggestion, determined the atomic weight of Japanese tellurium (T., 1896, **69**, 881), in the hope that this tellurium, which is associated with sulphur and not with any heavy metal, as is the case with European tellurium, might yield an atomic weight in conformity with the Periodic Law. The expectation, however, was not realised, the number obtained for the atomic weight of tellurium being 127·59, in close agreement with the values obtained in Europe.

In the lecture room, too, Divers always tried to avoid the use of hypothesis as much as possible, his Presidential Address on "Atomic Theory without Hypothesis," given to the Chemical Section of the British Association at its Belfast meeting in 1902, being a very interesting and faithful reflection of his mental attitude as a teacher. There was one theoretical question, however, which he used to discuss with much animation, and that was the theory of valency. The valency of an atom, according to Dr. Divers, represents the number of chemical reactions by which that atom parts with another atom or radicle united to it, and although in the case of a multivalent atom the second and succeeding steps often begin before the first is completed, thus giving rise to a mixture of products, each of the steps can, in some cases, be neatly followed, and the corresponding product easily isolated in a pure state. Thus, in the hydrolysis of nitrogentrisulphonic acid, the sulphonic groups are replaced by hydrogen one after another, and each of the three products, namely, imidodisulphonic acid, amidosulphonic acid, and ammonia, can be successively obtained unmixed with any of the other two.

Divers had two great misfortunes while in this country, and each of these gave him a very severe blow. The one was the sudden death of his son Frederic, which occurred in China, where he was in the service of the Maritime Customs under the late Sir Robert Hart, and the other was the loss of his beloved wife, Margaret Theresa, who died in Tokyo in 1897. After this, Divers never seemed to be in the best of spirits, and this fact, combined with his advancing age and isolation, led him ultimately to return to England in 1899. He was a most painstaking worker in whatever capacity his service was asked, and by his zeal and earnestness in the work he undertook, as well as by his straightforwardness, simpleness, and kindness, he won the respect and admiration of all who knew him well, among whom mention may be made of the late Prince Ito, who, in the early days of the old Engineering College, was the Minister of Public Works, and thus came in frequent contact with him.

The importance of Divers's service to the cause of education and learning in this country was early recognised by the Japanese Government, which, in 1886, conferred upon him the Order of Rising Sun of the Third Class, and again, in 1898, the Order of Sacred Treasure of the Second Class. In England, the Royal Society of London elected him a Fellow in 1885, in recognition of his important contributions to the general progress of chemistry, whilst in 1897 the Royal University of Ireland conferred upon him the honorary degree of Doctor of Science. He was further an Honorary Member of the Tokyo Chemical Society, the Society of Chemical Industry of Japan, and the Engineering Society, the last of which was established by those who were all Divers's students in the old Engineering College, and on his leaving Japan in 1899 the Imperial University of Tokyo conferred upon him the title of Emeritus Professor. In addition to these honours, a memorial bust of Dr. Divers was presented to the University by his old friends and pupils to be erected in the University grounds, and it was unveiled with due ceremony on November 17th, 1900 (compare *Chem. News*, 1900, **82**, 310).

On receiving the painful news of the death of Dr. Divers, the Imperial University at once sent a telegram of sympathy and condolence to his relatives, and a month after this, on May 10th, 1912, a meeting of his old friends and pupils was held in one of the halls of the University in his memory, when Prof. Haga, who is Dr. Divers's successor in the University, gave a memorial lecture (compare *Chem. News*, 1912, **105**, 275), which was afterwards printed in the *Journal* of the Tokyo Chemical Society.

Dr. Divers leaves behind him two daughters, both of whom were married in Japan, the elder, Edith, being married to Count Labry, who was a military attaché to the French Legation in Tokyo, and the younger, Ella, to Mr. E. W. Tilden, who was a resident of Kobe.

JOJI SAKURAI.

## HUMPHREY OWEN JONES, F.R.S.

BORN FEBRUARY 20TH, 1878; DIED AUGUST 15TH, 1912.

H. O. JONES was born at Goginan, in Cardiganshire, and came of that Welsh race which has given to Wales many of her most gifted and vigorous sons; this stock, which forms no inconsiderable part of the population in the district around his birthplace, has a strong Norse element blended with the earlier race. Up to seven years of age Welsh was his only speech. He first learnt English when his family removed their business to Ebbw Vale. Educated at Lewis's School, Pengarn, he entered the University College of Wales, Aberystwyth, with a scholarship in 1894, and graduated as Bachelor of Science in the newly constituted University of Wales at its first congregation in 1897. In the same year he gained a scholarship at Clare College, Cambridge, and entered that University as an affiliated student.

His record as an undergraduate is exceptionally brilliant. In 1899 he was placed in the first class in Part I of the Natural Science Tripos, and also obtained First Class Honours in Chemistry and Second Class Honours in Physics in the B.Sc. examination of the University of London. In the following year he received a First Class in Chemistry in Part II of the Tripos, with the very rare distinction of a "star." In 1904 he was admitted to D.Sc. of London University. While still "in statu pupillari," he had obtained (in 1901) a University official appointment, that of Demonstrator to the Jacksonian Professor of Natural Philosophy, Sir James Dewar, which he held up to the time of his death. He was elected in due course (1902) to a Fellowship at Clare, of which college he subsequently became lecturer.

For eleven years Jones devoted most of his time and energy to teaching in the University laboratory, and to the direction and supervision of the science students of his college. His main task in the chemical laboratory lay with undergraduates who were preparing for Part II of the Natural Science Tripos. It is in this work, perhaps, that he chiefly made his mark in the Chemistry School at Cambridge. It has been said of him that "for many years the advanced laboratory, where he was always at hand, practically revolved round him."

As a lecturer on organic chemistry Jones impressed his audience by the vast ground he was able to survey in the time at his disposal. His lectures, although not explanatory, were a model of concise expression. When, however, he was less constrained by shortness of time—in the lectures which he gave on his own special subject, stereochemistry—he got closely into touch with his audience, and could expound with a masterly lucidity. To the large elementary classes, as, for example, those he conducted for medical students, he was rather awe-inspiring; by a discipline which verged on the military, he made the class highly efficient.

But beyond this work with undergraduates Jones attracted a large and increasing number of graduates to carry on research under his direction. A long list of joint papers in various journals is evidence of his success with these students. He was not merely the teacher and director, but the guide and friend of the long succession of men who came under the influence of his vigorous and inspiring personality.

Jones was one of the most active and productive investigators of our day. In the last twelve years 1900–12, his name appears on no less than sixty separate publications. When the extent of his college and University duties was realised—he spent some five hours daily in the advanced laboratory, and was engaged for another two hours during term with the undergraduates of his college—it was not surprising to hear him say that a legal eight-hours' day would have made research impossible. Few, if any, were capable of such intense and continuous labour as he. In comparisons of the efforts of which men are capable, it was not uncommon to hear it said: "Jones is the hardest worker I have ever met."

Unlike many of his contemporaries, Jones had not visited foreign laboratories, or, in fact, other English Universities. He gained his experience of research entirely at Cambridge, working with Sir James Dewar and Dr. Fenton; with the latter he carried out his first experimental investigation on the "oxidation of organic acids in the presence of iron" (T., 1900, **77**, 69). In a short time he struck out on a line of his own—the Stereochemistry of Nitrogen—and in 1904 he prepared a report on this subject for the British Association. This report, which is of a peculiar excellence, shows at once Jones's great mastery of an intricate subject and his command of an exceptional lucidity of presentation. In 1907 and in 1909 he wrote the section on Stereochemistry for the annual reports of the Chemical Society. Whilst possessing the good qualities of his first publication, these later writings show in their selection and emphasis an increasing power of criticism. His familiarity with the important developments in chemistry other than his special subject, and his command of the methods of so-called "physical chemistry" appear in these monographs as well as in accounts of his experimental investigations. Although his exposition was never anything but lucid—was, indeed, often graphic—his style was sometimes inelegant. It was, however, free from all affectation or mannerism.

The study of organic nitrogen bases led to the attempt to solve the difficult problem of the constitution and transformations of the aldol bases derived from the homologues of aniline, an inquiry which he had proposed to follow up.

Jones's exceptional powers are well shown by the fact that, while engaged on his own particular branch of chemistry, he was assisting Prof. Sir James Dewar in investigations of a very different kind, namely, of the metallic (nickel and iron) carbonyls. These researches had made Jones familiar with low temperature manipulations. This led ultimately to their discovery of carbon monosulphide. It was undoubtedly in this way that Jones's attention was directed to organic sulphur compounds, and as a result he began the investigation of the thio-oxalates, thiomalonates, and thiophosphates. His eminence as an investigator was recognised in his election to the Royal Society last year, at the early age of thirty-four.

Jones's activities were not confined to teaching and research. The wider problems of University administration and educational policy increasingly occupied his attention; to him the practical life of the outside world and its relation to education was always a subject of great interest. The increasing calls upon him in these spheres of labour prove that his capacity was realised. He played a particularly active part in the recent extension and reorganisation of the chemical laboratory at Cambridge. As a co-opted member of the Cambridge Appointments Board, he found scope for his peculiar facility in taking the measure of a man; his opinion on a candidate could never be neglected and had already become highly valued by the firms who employed men on his recommendation.

The movement for which he was largely responsible, to bring the policy of the London educational authorities into harmony with University ideals, owes much of its promise of success to his energy and tact. Still further scope for his ability in affairs would have been found in the appointment, a few weeks before his death, to the Royal Commission to report on the use of oil fuel in the Royal Navy.

For several years Jones had few interests outside his work. He travelled a little, especially in Italy; he played golf, and was a member of the Cambridge and Royal Norfolk (Brancaster Links) Golf Clubs. He took great delight in gardening, and had a very good eye for the planting and laying out of grounds. A great and increasing interest was to arise when he discovered his peculiar power and inborn skill as a mountaineer—a discovery made almost accidentally in his native mountains as late as 1907. To this pursuit he brought all the thoroughness of his highly trained mind and the enthusiasm of his race. He set himself to learn the history of mountaineering, and to acquire the technique of the craft from the highest exponents, spending the greater part of his vacations in the Alps and in the mountains of North Wales. He soon developed a fine and accurate judgment of all the changing and varied conditions of the rocks, ice, and snow, and the weather of the Alps. Nothing seemed to escape his observation; he was the first to see the slight indications of changing weather or to recognise some rare bird or plant or some peculiarity in the rock formation. His knowledge of the Italian face of Mont Blanc was scarcely rivalled, and many new routes resulted from his thorough exploration of this region.

Nor was it only in intellectual power that his excellence was shown. Although his physique did not suggest muscular strength, he possessed a most remarkable endurance and the rare natural gift of a most delicate balance. His tirelessness and his speed are to be attributed, perhaps, not so much to inexhaustible vitality as to the economic use which his skill enabled him to make of his available force. His rapid, if not unique, rise to the very front rank of mountaineers was no surprise to those who had the opportunity of gauging the quality of the man.

He was elected a member of the Alpine Club in 1909, and was a member of the Committee of the Climbers' Club. The journals of both clubs, but especially of the Alpine Club, contain several papers in which his many daring explorations are recorded.

The very fact that he had passed over in so short a period the early stages in his initiation to mountaineering perhaps distantly contributed to the accident in which he and his bride were killed. He did not take into account the possibility of a native Alpine guide slipping on an easy place. Whilst ascending the north ridge of the Mont Rouge de Peteret, near Courmayeur, on Thursday, August 15th, 1912, their guide slipped and fell on Jones; the three dropped nearly 1000 feet to the Fresnay Glacier.

He married, on August 1st, 1912, Muriel Gwendolen Edwards, a member of the family to which the Bishop of St. Asaph and the late Dean of Bangor belong. She was a woman of great force and vitality, with rare gifts of taste and perception. A member of Newnham College, she had made chemistry her subject, and was the first woman to be elected a Fellow of the University of Wales. As enthusiastic as her husband in her love of the mountains, she appeared to their friends the perfect comrade for him in the intense life which opened before them.

The circumstances of Jones's life at Cambridge, and more especially his mountaineering, provided the opportunity for his characteristic genius for friendship. He was on terms of intimacy with a large number of men with whom his varied interests had brought him in contact, or who were attracted by his sympathetic temperament.

Remarkable as is the extent of his original work, it is yet difficult to decide whether Jones would have developed, as he gained more leisure and freedom, into a great original thinker and experimentalist. Perhaps because of his many abilities, his alertness, and his versatility, he tended to take up new and varied interests rather than to become entirely absorbed in his research. Jones was essentially a teacher; he took a minute personal interest in his students, and was never tired of discussing their characteristics and particular abilities, a quality which made him an excellent examiner. His ready sympathy and delicate tact made him easy of approach; few men were so often consulted or gave sounder advice.

That he was a man destined to exert a powerful influence in educational and scientific affairs, and to attain the highest eminence in University life there can be little doubt. The splendid tribute which is now being offered to his memory by a number of important firms, as well as by Cambridge colleagues and private friends, attest the esteem in which his character and intellect were held, and the value which was placed upon his training, as well as on his judgment, of men.

K. J. P. ORTON.

# JOHN WILLIAM MALLET.

BORN OCTOBER 10TH, 1832; DIED NOVEMBER 7TH, 1912.

THOSE who were so fortunate as to have seen Professor Mallet at the meeting of the Eighth International Congress of Applied Chemistry, at New York, were not prepared for the sad news of his death so soon afterwards, on November 7th, 1912; for in September he had seemed in good health. His illness was brief, and he died in Charlottesville, Virginia, where he had lived so many years. With his going, another of that older generation of chemists, who have done so much to make chemistry a power in the world, passes away; the world misses them keenly.

John William Mallet was born near Dublin, Ireland, on October 10th, 1832, the son of Robert and Cordelia Mallet. His father was a civil engineer, and Fellow of the Royal and other scientific Societies; and the son's interest in chemistry was early acquired from the reading of chemical classics in his father's library when a schoolboy. Before entering college he received private instruction in chemistry from Dr. James Apjohn, and at the age of seventeen he was admitted to Trinity, Dublin, where he obtained the degree of Bachelor of Arts in 1853, as gold medallist in Experimental Physics. The intervening years were profitably spent in a manner very different from that of the average collegian. His first paper on "A Chemical Examination of Killinite" was published in 1849, soon after his admission to college; and much time during the following years was spent in assisting his father in seismological investigations. During the summers of 1851 and 1852 he went to the University of Göttingen, where he studied chemistry under Wöhler, and received the degree of Ph.D. in 1852. He presented a thesis concerning the chemical composition of the Celtic antiquities in the Museum of the Royal Irish Academy.

After returning to and graduating at Trinity College, he went, for the purpose of acquiring information for his father, to the United States; but he never became a naturalised American, remaining a British subject to the end. He was soon appointed professor of analytical chemistry at Amherst (1854), where a Göttingen friend, Dr. W. S. Clark, was in charge; but the following January Mallet accepted the position of chemist to the State Geological Survey at Tuscaloosa, Alabama. This change greatly influenced his life, for from that time forth his interest was allied with the South rather than with the North. In 1855 he became professor of chemistry in the University of Alabama, serving in that

capacity, with a brief leave of absence spent at Mobile, until the opening of the great Civil War. In the autumn of 1861 he enlisted as a private in a troop of Confederate Cavalry, but almost immediately was chosen as aide-de-camp on the staff of General Rodes. He was soon transferred to the artillery in May, 1862, and was in rapid succession captain, major, lieutenant-colonel, and later superintendent of the ordnance laboratories of the Southern States, from 1862 to 1865. His service to the Confederacy in supervising the manufacture of gunpowder was very great; he showed courage, wisdom, and patience in this task. In 1865, just before the close of the war, he was paroled as lieutenant-colonel of the artillery.

After peace had been established he became professor of chemistry in the medical department of the University of Louisiana. The appointment was the outcome of a mission which he undertook, on behalf of some Northern financiers, to search for petroleum in this southern state. The result of the appointment was to direct his attention to medicine, in which he gained the degree of Doctor in 1868. In that year he was called to the University of Virginia, which became his final home, although not uninterruptedly. At first his work included analytical, industrial, and agricultural chemistry, but, as time progressed, his scope became broader and broader. He lectured at Johns Hopkins in 1877 and again in 1878, and during the winter of 1883–84 was professor of chemistry and physics, and chairman of the faculty in the University of Texas. The following year found him at the Jefferson Medical College in Philadelphia as professor of chemistry, but the unsatisfactory conditions there caused him to return in 1885 to the University of Virginia, which he never again left. In 1908 he was appointed professor emeritus at the age of seventy-six, but still kept his residence at Charlottesville, the beautiful seat of the university founded by Thomas Jefferson long ago.

Besides his services to the Southern States during the war, he undertook a number of other commissions of a public or semipublic nature, having served as judge in the bureau of awards at the Centennial Exposition in 1876 and been a member of the United States Federal Assay Commission in three years, 1886, 1888, and 1896. These last appointments showed that he and the Government had generously outlived the jealousies of the war. He belonged to many chemical and other learned societies besides the Chemical Society, being an honorary member of a number of them. He was a fellow of the Royal Society, of the College of Physicians of Philadelphia, of the Medical Society of Virginia; associate fellow of the American Academy of Arts and Sciences, and fellow of the American Association for the Advancement of Science, member of the Society of Arts in London, American Chemical Society (of which he was President in 1882), Chemical Society of France, German Chemical Society, American Philosophical Society of Philadelphia, and several other local societies, including several in Mexico and Brazil. He received the honorary degree of LL.D. from five institutions of learning, namely, William and Mary College, University of Mississippi, Princeton, Johns Hopkins, and the University of Pennsylvania.

His interest in the South was emphasised and strengthened by his marriage to Mary E. Ormond, the daughter of an Alabama judge, in 1857, and again, after the death of his first wife in 1886, to Mrs. Joséphine (Pagès) Burthe, of Louisiana, in 1888, who with two of the three children by his first wife survives him. His first-born son, John Ormond Mallet, died at an early age.

The scientific work of Professor Mallet covered a wide field. Besides his studies in general and applied chemistry and in chemical mineralogy, which were incidents in his work for the Southern States and in various technical professorships which he held, he spent much time on various other analytical problems of interest; for example, he devised methods for the determination of organic matter in potable water. He added to our knowledge of meteorites, and of many rare terrestrial minerals, by careful analysis. He studied the occurrence of silver in volcanic ash from South American valcanoes. Theoretical problems also interested him greatly; for example, he determined the density of solid mercury and the molecular weight of hydrofluoric acid. He probably will be remembered chiefly in the field of pure chemistry through his work on the atomic weights of lithium, aluminium, and gold. The work on aluminium was particularly comprehensive and thorough, and has remained our chief basis for a knowledge of this atomic weight ever since its publication in 1880. The work on lithium, one of the first investigations in a field which has since been very much cultivated in America, was carried out in 1856. It is interesting to note that this work, although somewhat crude, was far better than that of Stas, as indicated by the most recent investigation of this subject. His value 6·943 is very near the value which at present seems most probable, namely, 6·939, whereas Stas found the widely-divergent number 7·01, making mistakes in this case perhaps more serious than in any other. Mallet's interest in atomic weights appeared also in the admirable lecture delivered in memory of J. S. Stas in 1892 by request of the Chemical Society. Besides all this purely scientific accomplishment, he carried out a large amount of technical and expert work. He served as expert witness in many medico-legal cases involving various forms of poisoning, as well as took part in numerous commercial cases involving the value of iron ore, the pollution of river water, and many other chemical questions. As analytical and consulting chemist also, he performed many analyses and gave advice concerning a great variety of chemical processes, doubtless adding much to the efficiency of his client's undertakings.

This brief record does but scanty justice to a life full of manifold usefulness and high endeavour. A more complete biography and a complete bibliography of Dr. Mallet's publications is to be found in the January (1913) issue of the sixth volume of the Alumni Bulletin of the University of Virginia. Out of this paper the following extract from a vote of the Faculty of the University is reprinted:

"He stood like a rock for principle, high character, truth, and integrity. His influence has been for courage, strength, and steadfastness of purpose to meet the problems of life earnestly and hopefully. Great as have been his world-wide acknowledged intellectual achievements in science, these seem to fade into insignificance when compared with the impress of character which he has stamped upon the generation of men who have sat at his feet in this University. He was the soul of honour, truth, and courage; he hated sham, deceit, and charlatanism in all their forms, and, regardless of the consequences, never permitted himself to swerve a hairbreadth from what he recognised to be a principle. He lived his life before all men as a manly man and a kindly gentleman without fear and above reproach."

THEODORE W. RICHARDS.

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## HENRY DE MOSENTHAL.

BORN 1850; DIED DECEMBER 17TH, 1912.

HENRY DE MOSENTHAL was born at Port Elisabeth, South Africa, in 1850, and died on December 17th last. During the greater part of his life he was connected with the explosives industry, having been technical secretary to the Nobel Dynamite Trust Company, Ltd., since its formation. For many years previously he had associated with Alfred Nobel, the inventor of dynamite, and many of his researches had reference to the explosives industry. De Mosenthal was an expert microscopist, as well as an experienced technical chemist, and his investigations have contributed much to the progress of the industry with which he was associated. Most of his papers were read before the Society of Chemical Industry, and were published in the *Journal* of that Society. Among the more important of these may be mentioned "Observations on Cotton and Nitrated Cotton," published in 1904, 1907, and 1911. A visit to South Africa furnished the material for an interesting paper on the "Treatment of Gold Ores at the Witwatersrand (Transvaal) Gold Fields," published in the *Journal* of the Society of Chemical Industry, 1894. Besides his published researches, De Mosenthal undertook many other investigations in industrial chemistry, which were not published. One of these was a careful inquiry into the occurrence of deposits of saltpetre in South Africa, and he also made an exhaustive inquiry into the methods by which a less inflammable substitute for celluloid could be produced. De Mosenthal's researches were extended beyond the limits of pure and applied chemistry, one of his earliest papers being on the structure of the eye, a contribution to science which was enriched by numerous excellent microphotographs. A shrewd observer and a good linguist who had travelled much, De Mosenthal was an excellent conversationalist. He was a bachelor and a member of the Savage Club.

W. F. REID.

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## BENJAMIN EDWARD REINA NEWLANDS.

BORN JANUARY 23RD, 1842; DIED AUGUST 7TH, 1912.

BENJAMIN EDWARD REINA NEWLANDS, youngest son of the Rev. William Newlands, was born at Southwark on January 23rd, 1842. His mother was of Italian descent. Both he and his brother John (who will be remembered in connexion with the discovery of the periodic law of the elements) studied under Professor A. W. Hofmann at the College of Chemistry, and at an early age they started in practice as analytical chemists in London. Benjamin became an assistant to Professor Heaton at Charing Cross Hospital in 1862 and to Professor Way, of the Royal Agricultural Society, in 1863. His bent was always, however, towards technology, and at the end of 1863 he was appointed chemist to Messrs. J. Gibbs and Co., manure makers, Victoria Docks. He held the appointment of manager at this works from 1869 to 1873, after which year he became manager at Messrs. J. Duncan's sugar refinery, Clyde Wharf, Victoria Docks, his brother John being chief chemist. This position he retained until the close of the refinery (then the largest in the United Kingdom) in 1887, when the brothers once more embarked upon a professional career as analytical and consulting chemists. Well known as they were in the sugar industry, the brothers Newlands soon built up a good practice, chiefly concerned with sugar technology, not only of this country but also of the

Colonies and India. After the death of John Newlands, the writer was in partnership with Benjamin for five years. Benjamin Newlands was a very active member of the Society of Chemical Industry, having served on its Council and most of its committees from its inception. He will be remembered by his professional brethren for his wide practical knowledge no less than for his sound common sense, which was tempered by a characteristic and rare geniality of manner.

ARTHUR R. LING.

## JOHN PATTINSON.

BORN FEBRUARY 13TH, 1828; DIED MARCH 28TH, 1912.

JOHN PATTINSON was born at Alston, in Cumberland, on February 13th, 1828. He spent his schooldays at the Grammar School there, and whilst he was quite a youth his distant kinsman, Hugh Lee Pattinson, well known as the inventor of the Pattinson process for desilverising lead, invited him to come to Newcastle, and placed him in the laboratory of the Felling Chemical Works on the Tyne, where the manufacture of alkali by the old Leblanc process was carried on, with its attendant manufactures of sulphuric acid, hydrochloric acid, and bleaching powder. After ten years' association with the alkali manufacture, John Pattinson went to Middlesbrough under Isaac Lowthian Bell; and he there acquired an intimate knowledge of the iron and steel manufacture as it was practised in these early days—the days when Bell was beginning that long series of researches which were collected later in his classic "Chemical Phenomena of Iron Smelting." In 1858, Pattinson left Middlesbrough and returned to Newcastle, where he took over the practice of analytical and consulting chemist then carried on by William Crowder, in the Side, and in that work, with two successive removals to larger premises, he continued until his death. In 1890 he was joined in partnership by his eldest son, Dr. H. S. Pattinson (died 1904), and in 1901 by the present writer. In 1868 he was instrumental, along with his brother-in-law, Mr. J. W. (now Sir Joseph) Swan, the late Barnard Proctor, and others, in founding the Newcastle Chemical Society, which had a useful and honourable career until, in 1882, it merged its separate existence in the Society of Chemical Industry; he was treasurer of that Society during the whole fourteen years of its existence, was its president during 1874-75, and published papers in its Transactions on the determination of peroxide of manganese, on the quality of the small coal used on the Tyne, on the determination of arsenic in copper, and other subjects. At the meeting of the British Association in Newcastle in 1863, he read a paper on the pyrites used on the Tyne; he was also a member of a Committee of that Association on the question of the illuminating power of coal gas. His firm having a large practice in the assay of iron and manganese ores, he was led to investigate the conditions under which manganese can be precipitated as peroxide, and described before this Society in 1879 a method for manganese determination, which is still in daily use in laboratories where these determinations are made, and is of great accuracy and trustworthiness. Several other papers and notes by him alone, or with H. L. Pattinson or J. T. Dunn, are found in the Society of Chemical Industry's *Journal*. He was among the earliest to hold municipal appointments connected with chemistry—he was made Gas and Water Examiner for Newcastle in 1863, and Food Analyst in 1871; later, when the Food and Drugs Act of 1875 was passed, he was appointed Public Analyst for Newcastle, for the County of Northumberland, and for other boroughs near. He was a Fellow of this Society since 1863, and had been a Vice-President, and a Vice-President of the Society of Public Analysts; was an original Fellow of the Institute, for which he had served on the Council and as Censor; was an original member of the Iron and Steel Institute; and was a Vice-President of the Literary and Philosophical Society of Newcastle.

He was a man of very varied activities outside his profession—a Justice of the Peace, and an administrator in various philanthropic and charitable institutions; an enthusiastic musician, and president of the local Choral Union; and had the high esteem of all who came into contact with him, no less for his kindliness of disposition than for his incorruptible uprightness and straightforwardness.

J. T. Dunn.

## ARTHUR RICHARDSON.

Born 1858; Died June 1st, 1912.

Dr. Arthur Richardson was born in 1858, and belonged to a well-known Quaker family. He was elected a Fellow of the Chemical Society in 1885. He first studied chemistry under Prof. Crum Brown in the University of Edinburgh, but when in 1876 Dr. E. A. Letts was elected to the Professorship of Chemistry at the University of Bristol, he entered as a chemical student under Prof. Letts. In 1883 he spent a year under Prof. Wislicenus in Würzburg. In 1886 he obtained the Ph.D. degree at Freiburg University, and he then returned to University College, Bristol, as an assistant, remaining there until 1896. In 1888 he was made an Associate of University College, Bristol. Leaving Bristol in 1896, he went to India, associating himself with the cult of Esoteric Buddhism, and gave up the remainder of his life to work connected with teaching at the Central Hindu College, Benares. There he taught chemistry, and for many years was head of the College.

During the last ten years of his life, owing to growing ill-health and lack of opportunity, he did little research, but he was always keenly interested in what was going on in the chemical world.

It was before he left England that the most important of his investigations were carried out. These mostly centred round one idea—the action of light on various substances; and on this subject he published a good many papers. His best piece of work was on the measurement of light intensity by the expansion of chlorine when exposed to sunlight, and he constructed an automatic registering apparatus that would record continuously the actinic intensity of the light under all conditions of weather throughout the year. Several other papers were of considerable interest: the action of light on the hydracids in presence of oxygen, the decomposition of silver chloride under the influence of light, and the action of heat on nitrogen peroxide, were all excellent work. Dr. Richardson was a true investigator, but he was always far more interested in the mechanism of reactions than in the manufacture of new substances; nevertheless he was an expert worker, and many of his pieces of apparatus were marvels of ingenuity. J. N. Collie.

## JOHN WADE.

Born January 13th, 1864; Died August 15th, 1912.

John Wade was born at Deptford on January 13th, 1864. A tragic accident which he suffered on the 28th of July last year brought to its end a life still in its prime and full of the promise of further achievement. Wade was riding a motor-cycle at Otford when he collided with a cart which had suddenly turned a corner of the road. A shaft struck him violently in the upper part of the chest, fracturing four ribs and damaging a lung. After surviving for three weeks and giving his friends good reason to hope for his ultimate recovery, he died suddenly on August 15th, 1912, as the result of a pulmonary embolism.

To appraise with full justice Wade's accomplishment as a scientific worker and teacher, it is necessary to realise that he was intellectually, self-made. In his scientific development he owed to others as little as it is possible for any man to owe. Wade's father was a highly intellectual man, of pronounced artistic tastes, and no small power of artistic accomplishment. He had a circle of cultured friends, and John Wade had the advantage, when a youth, of living in a cultured household. But his father, who depended upon his salary as an official of the Kent Water Works Company, was unable to afford him any but an inexpensive education, which had to stop when his schooldays, spent at Aske's School, Hatcham, came to an end.

He entered, when a youngster of less than sixteen, the private laboratory of Sir Thomas (then Dr.) Stevenson, at Guy's Hospital, prepared to make himself generally useful. He found there Mr. Richard Bodmer, the present Public Analyst for Bermondsey and Northampton, who was then, and for many years afterwards, Dr. Stevenson's private assistant. Wade's career was not then chosen, and he went to the laboratory without definite aims, and merely to await developments. The first development came when the then lecture assistant at Guy's lost his reason and offered personal violence to the lecturers. Wade temporarily filled the gap thus rendered inevitable, and after a very short interval of, at most, a few months, spent in the laboratories of the Royal College of Science, he was definitely appointed to the office, and remained in it for about six years.

The only educational scientific lectures he ever attended—save a few connected with evening classes at the Birkbeck Institute—were those he thus heard as an untaught lecture assistant, and so far as he listened to them at all it was as a youth not yet aware that chemistry was to remain his life's pursuit. He was privileged, it is true, to assist such able teachers as Debus, Thomas Stevenson, Charles Edward Groves, and Reinold, and doubtless such contact as he had with them carried inspiration; but all were busy men of whom Wade saw little in the laboratory, and with whom his relations were of a quite formal sort. He never, at any time of his life, even saw a foreign laboratory, and never once shared the responsibility of research with a senior; never, indeed, saw any research in progress save that inspired by himself.

For a year or two after his appointment as lecture assistant he made no attempt to acquire any real knowledge of chemistry, being but a prankish boy, although a very clever one. He was somewhat plagued at this time by a mountain of flesh, weighing twelve stone when only sixteen. Although he completely got rid of this trouble later on, it was only kept under by careful habits in diet. By 1883 his intellectual development had greatly progressed, and he began to take serious thought for the future. He gave his evenings to successful study for London Matriculation, and afterwards attended classes at the Birkbeck Institute while preparing for the Intermediate Science Examination. In 1886 he gave up the position of lecture assistant, and, for the moment, gave up also all idea of a scientific career. He thought of entering the Patent Office, and worked for a while in preparation for the necessary examinations. A little later he had some notion of a non-collegiate course at Cambridge, and resided in the town for a few weeks during Long Vacation; but he experienced some discouragement, and gave up the enterprise. At this period his mind was much unsettled; he felt he was marking time, and was, not unnaturally, depressed. He spent a little time in the laboratory of F. J. Lloyd, and for about a year was chemist in a paper works at Northfleet. In 1890, having been a little earlier appointed Gas Examiner under the London County Council, he entered into partnership with his earliest colleague, Richard Bodmer, and shared for a year his laboratory in Southwark Street. About this time Wade took the B.Sc. degree.

Meanwhile his merits had not been overlooked or forgotten at Guy's, and when, in 1893, Groves ceased to participate in the practical teaching, and the appointment of an Official Demonstrator became necessary, the authorities of the medical school sought Wade's services. He accepted the post with delight, and now, for the first time, felt that ease of mind which comes with security and a defined aim. Retaining his Gas Examinership, he felt able to marry, and took to wife Clara Threadgold. He lived first at Purley, but later, in order to be near his work, he settled in Trinity Square, S.E., and remained there until, in recent years, he went to live at Downe.

It should be understood that, not until the time of his appointment as Demonstrator at Guy's, when he was already twenty-seven years old, did Wade's mind come seriously to grips with the subject he was to know so well and teach so admirably.

He set to work to organise the practical teaching of the medical school laboratories on original and stimulating lines, and, when he felt that this task had been accomplished, he began to gather material for his text-book. During the slow writing of this book, which he accomplished with infinite pains and labour, Wade made himself a profoundly learned organic chemist. He went to original sources for every fact, and being gifted with a most retentive memory, and an active imagination, he stored an immense amount of knowledge, and at the same time was greatly stimulated by prolonged contact with the original writings of master chemists. His marked critical power and sense of proportion marshalled the facts of the science into an ordered edifice within his mind, and he became, as I have claimed, really learned in his subject. He produced an admirable book, but, what is more important, the writing of the book made its author an enthusiast. The first edition of the book appeared in 1897, the second in 1905, and the third in 1911. It has been translated into other languages, including Portuguese. Wade became joint lecturer on chemistry in 1898, and in 1901, on the retirement of Mr. Groves, he became sole lecturer and head of the Department.

Wade had skilful hands and an instinct for accuracy in all kinds of experimental work. In his earlier days as a responsible teacher, he spent an immense amount of time in rehearsing and testing methods, and much labour spent in improving them never had the reward of publication. He was amply stocked with ideas, and began research immediately after he had commenced to write his book; but, as I shall later point out, his preoccupations and his temperament made original work for some years very difficult.

He was early interested in the question of the constitution of hydrocyanic acid, and, like many others, possessed at one time the hope of being able to prepare its unknown isomeride. As the first-fruits of work done in this connexion, he published, with L. C. Panting, in 1898, a brief paper, in which it was shown that in the action of sulphuric acid on potassium cyanide, a practically quantitative yield of either hydrocyanic acid or carbon monoxide respectively can be obtained by suitably varying the concentration of the acid (T., 1898, **73**, 255). In 1900 appeared a note on the constitution of hydrocyanic acid, which was eventually expanded into the highly important paper (T., 1902, **81**, 1596), "On the Constitution of Metallic Cyanides as deduced from their Synthetic Interactions." Dealing with the familiar circumstance that while the alkali cyanides when reacting with alkyl sulphates or iodides yield nitriles, the cyanides of the heavy metals yield in similar circumstances alkyl *iso*cyanides, Wade showed that it is logically impossible to explain the facts by assuming the occurrence of isomeric change or by means of Laar's hypothesis of tautomerism in the molecule of hydrocyanic acid. Having shown that all the evidence goes nevertheless to prove that the alkali cyanides, no less than silver cyanide, have themselves the carbylamine structure (although hydrocyanic acid is a nitrile), he explained all the phenomena involved by an ingenious extension of Nef's hypothesis concerning the intermediate formation of additive compounds. The paper contains an account of abundant original experimental work, some of which illustrates the author's genius for defining the exact experimental conditions necessary to produce a desired result.

Wade's subsequent work dealt for the most part with physical chemistry, and was mainly concerned with the properties of mixtures with a constant boiling-point. Various circumstances directed his efforts into this channel. The subject appealed first of all to an intellectual prepossession which finds reference below. Then, in his cyanide work, he came upon a case which impressed him with the practical importance of these mixtures. He at one time thought he had successfully separated nitriles from *iso*cyanides by fractional distillation, but later found that the supposed *iso*cyanide fractions were really hylotropic mixtures of nitriles, alcohols, and hydrocyanic acid, containing but little of the *iso*cyanides (compare P., 1900, **16**, 156; T., 1902, **81**, 1598). Again, in 1904, he had undertaken, in conjunction with H. Finnemore, to find an explanation for the fact that chloroform made from acetone had properties as a practical anæsthetic mysteriously inferior to those of the product from alcohol. The practical end of the research was attained when it was found that the latter always contained traces of ethyl chloride which improved its anæsthetic action, and when it was shown that the addition of the same substance to "acetone chloroform" brought it into line with the alcohol product. In the course of the very interesting work involved in this investigation (T., 1904, **85**, 938) Wade isolated several ternary and binary mixtures, gaining great skill in fractional distillation and an increased interest in the subject. In the following year he published a paper on the influence of water and alcohol on the boiling point of esters (T., 1905, **87**, 1656). In this is first described a method for the preparation of esters by a continuous process, and next a very careful quantitative study of the fractional distillation of ethyl acetate in the presence of alcohol and water, during which ternary and binary mixtures of constant boiling point were isolated, and their properties studied.

In 1909 Wade and Finnemore turned their attention to ethyl ether, having observed that while the boiling points found for this substance by modern observers were concordant, the variations in the statements as to its density lay outside the limits of experimental error. The outcome of the work (T., 1909, **95**, 1842) was a proof that ether forms a binary mixture with water, which boils, with characteristic constancy, 0·35° lower than pure ether. Unless therefore all but traces of water is first removed, it is impossible to prepare the pure substance by fractional distillation. Ternary hylotropic mixtures of alcohol, water, and ether were shown not to exist, but the presence of alcohol was found to raise the boiling point of the above binary mixture as well as of ether itself.

During these various studies of fractional distillation, Wade wished to determine the specific gravity of individual fractions with the highest possible accuracy, but found it difficult, in spite of great experimental care, to obtain results concordant within the required limits. He traced the errors to an inadequacy in the formula ordinarily used for correcting for the buoyancy of air, and in a paper published with R. W. Merriman, who had become his Demonstrator, he describes some careful experimental work done in connexion with this matter, and proposed a new correction formula which yields satisfactory values (T., 1909, **95**, 2174). By this time, having realised by experience the difficulties which occur in the endeavour to isolate constant mixtures of minimum boiling point, and wishing in particular to study the effect of variations in pressure on the physico-chemical "individuals" which were interesting him, Wade felt the need of special apparatus. His needs led him to construct the "manostat," as he called it, an instrument capable of continuously maintaining in the distillation apparatus pressures high or low with a maximum deviation of ±0·2 mm. from the mean. In the paper which describes this (Wade and Merriman, T., 1911, **99**, 984), other very ingenious adaptations of apparatus to the requirements of the problem will be found. Wade and Merriman (*ibid.*, 997) now submitted mixtures of alcohol and water to distillation under various pressures. They found that the composition of the constant boiling-point mixtures ("azeotropic," or temporarily hylotropic mixtures, as it was now proposed to call them) varied continuously with pressure, and they got no indications, at any time, of the transition of such a mixture into a more permanently hylotropic substance ("chemical individual") on the lines of suggestions by Wald and Ostwald (Ostwald, T., 1904, **85**, 511). They found that in the case of mixtures of minimal boiling point the percentage of water present increased with the pressure, whilst they got evidence that at pressures below 100 mm. no azeotropic mixtures of alcohol and water are formed at all, so that it should be possible to obtain anhydrous alcohol by fractional distillation at such low pressures. In a large scale rectifying apparatus, they point out, it is possible to reduce the percentage of water to a fraction of 1 per cent. by one or two rectifications under 50 mm. pressure.

The remaining papers were published after Wade's death by his colleague, Mr. Merriman (T., 1912, **101**, 2429, 2438). They contain an account of the purification, density, expansion, and vapour-pressures of ethyl acetate, the work described showing the meticulous care and experimental resourcefulness of all that had preceded it.

Everyone will admit that the quality of Wade's scientific work was of a high order and worthy of his undoubted genius; but it may be felt that its actual amount was not proportionate to his characteristic industry. If this be true, it is because his output was limited by his temperament and by the large amount of extraneous work in which he engaged. He inherited his father's artistic temperament, and it made him crave for a finality and perfection in his work which in a scientific investigation is so rarely possible. He always hesitated to publish, even when his note-books were full.

On the other hand, for some years he spent a great deal of time on very admirable work done for the Local Government Board in connexion with the subject of ship disinfection (*Brit. Local Govt.*

*Bd. Rep.*, 1907), and, as is well known, he devoted himself continuously to the politics of the London University. In his opposition to the concentration of Preliminary Science teaching, he was moved by the belief that it was against the interests of the medical schools as institutions, no less than those of the teacher and the taught; and he was able to convert the majority to his opinion. The strong support he gave to the maintenance of the External Side of the University arose partly from sentiment—for he was strongly indebted to that side—but it was based also upon thought and conviction. He was able to give impressive evidence in its favour before the Haldane Commission. He gave his time to those controversies from a sense of duty, but it must be admitted that he took a pleasure in fighting for his beliefs; for, combined with his artistic inheritance, he carried a temperamental legacy of a quite different kind. His paternal grandfather was, in his time, a keen politician, and a noted protagonist in the struggle for civil and religious liberty in South London. There is no doubt that John Wade enjoyed being in the arena almost as much as he enjoyed giving attention to the fifth decimal place in his laboratory work. In fact, the combination in him of the artist, scientist, and man of affairs was somewhat remarkable; the various sides of him were not always known to the same people.

As a scientific thinker Wade was especially characterised by an earnest belief that chemistry ought to be liberated from the shackles of atomistic hypotheses. He held that all the stoicheiometric laws and all that is special in chemical phenomena are capable of explanation from a dynamical point of view. I must point out that he held these views when quite young, long before Ostwald had delivered his Faraday lecture in 1904, and before the writings of Franz Wald (that "solitary philosopher," as Ostwald calls him) were known to him. I remember hearing Wade expound his views in 1895, and I realised then, as often later on, how great was his tendency to be preoccupied with the widest and most general aspects of his science.* He always intended that his own researches should bear upon the above great matter; hence his great interest in hylotropic mixtures, which, had he been spared, were to have received much more attention at his hands. The sorrow felt by his friends for his tragic death was intensified by their knowledge of the fact that, freed from his preoccupations, and recently provided with an admirably efficient laboratory, he was beginning what might well have proved the most prolific period of his life as an investigator. His mind remained alert and elastic, and his energy and enthusiasm were unabated.

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* I venture to quote the above paragraph from an article written by myself in the *Guy's Hospital Gazette* for August 31, 1912.

Wade became a Fellow of the Chemical Society in 1890. He was a member of the Council from 1905 to 1909, and served upon the Publication Committee. He was admitted Fellow of the Institute of Chemistry in 1891, and received the Doctorate of the London University in 1902. He leaves a widow and one son—a youth of great promise.

F. Gowland Hopkins.

## WILLIAM ORD WOOTTON.

Born October 5th, 1884; Died October 17th, 1912.

By the premature death of this promising young chemist our science has lost one of its most enthusiastic workers. A son of the late Staff Engineer W. W. Wootton, R.N., he was born at Portsmouth on October 5th, 1884. He was educated at Sir Joseph Williamson's Mathematical School, Rochester, where he became Head of the School. Having gained the Governors' Leaving Exhibition, he spent a short time at the Birkbeck College, and in 1902 he entered the Royal College of Science at South Kensington. Having passed with distinction through the curriculum, he was appointed, three years later, one of the "teaching scholars," and in that capacity assisted in giving practical instruction in the laboratory of the college. About the same time he took the degree of B.Sc.Lond., with honours in chemistry. In 1906 he was promoted to the position of one of the assistant demonstrators at the time of the removal of the chemical department to the new buildings. In 1910 he was chosen to fill the vacant post of Demonstrator at St. Bartholomew's Hospital Medical School, and there he remained until seized with fatal illness. He died on October 17th, 1912.

Mr. Wootton was a born investigator. His interest in science began to show itself early in his school career, and after he became a student at the Royal College of Science he soon attracted the notice of his teachers by his intelligent and ardent devotion to experimental work.

His first independent investigation was embodied in a paper on "Aromatic Amides and Imides," which appears in the Transactions of the Chemical Society for 1907. Other papers followed in 1910 and 1911, also in the Transactions. Possessed of an ever active mind, he was never so happy as when engaged on new problems, and this enthusiasm he was often able to communicate to the students under his charge, and by whom he was much esteemed and respected.

His family wish it to be known that he was to the last a devout member of the Church of England. His last distressing illness, which he knew to be hopeless, he bore without complaint and with quiet fortitude.

W. A. T.

# LXXVIII.—*The Action of Tartaric Acid on Tin in the Presence of Oxygen.*

### By Alfred Chaston Chapman.

In connexion with a technical investigation with which I was concerned four years ago, I had occasion to ascertain the effect of aqueous solutions of tartaric acid on tin under varying conditions. In the course of the work I noticed certain phenomena which I could not understand, and which appeared to me to be of sufficient interest to justify a more detailed and systematic study of the reactions involved. To this end I decided partly to immerse rods of pure tin in moderately dilute aqueous solutions of the acid, and as the action was to take place at the ordinary temperature and would be a very slow one, I thought that the most convenient method of conducting the experiments would be to employ deep wide-mouth bottles closed with corks, the tin rods being passed through holes bored in the corks, and so held in a vertical position in the acid solution. The bottles had a capacity of about 150 c.c., and in each there was one rod. It should be stated that in all cases the corks were bored entirely through, and a very short length of each rod projected as a rule above the top of the cork. Twenty of the bottles contained a 5 per cent. solution of the pure acid in distilled water, whilst in five a 10 per cent. solution was employed. The tin was the purest supplied by Kahlbaum, and on analysis was found to contain only minute traces of impurities. The rods were approximately 7 mm. in diameter, and the length actually immersed in the liquid was usually about 10 cm. The bottles contained the acid solution to the level of their shoulders, so that when the cork with its rod of tin was inserted, each bottle contained a few c.c. of air between the level of the liquid and the bottom of the cork. I have felt it necessary to enter into these details, since they have an important bearing on the results obtained. The bottles were all exposed to full daylight and kept at ordinary atmospheric temperatures. At the end of some months the surfaces of the rods were seen to be distinctly etched, and later small, colourless crystals formed on some of the rods. Similar crystals also occurred at the bottom of some of the bottles, and at the time I thought that these had become detached from the rods. Later I found that, although this did account for some, there could be no doubt that a proportion of the crystals had never formed on the surface of the metal. The action was evidently a very slow one, and the bottles were left unopened for about three years. At the end of that time it was found that in the bottles containing the 10 per cent. solution of the acid very little action had occurred, and in no case had the crystals formed as readily as in the weaker solutions.

In the light of what was subsequently learned as to the nature of this action, it will be seen that this may have been to some extent a matter of accident. The bottles containing the weaker acid could be divided into three groups: (1) Those in which no apparent action had taken place, the tin rods being perfectly bright, though sometimes slightly etched, and the contents of the bottles entirely free from crystals. (2) Those in which the tin had obviously been very much acted on, the rods being more or less covered with well-formed crystals, whilst in some a further amount of crystalline deposit occurred at the bottom of the bottles. In these cases the acid solution was colourless, and had very little odour. (3) In these the tin had been very considerably acted on, the rods being closely coated with crystals, which were, as a rule, smaller and less well defined than those in the preceding group. In four of the bottles the rods had been completely eaten through at the surface of the liquid, and the acid solution was distinctly coloured, the colour ranging from a pale straw colour to a deep orange-red with a slight greenish fluorescence. These solutions had a distinct odour suggestive of slightly charred sugar. At first I thought that the different behaviour of the metal in these various experiments might be due to slight differences in purity, but very careful analysis showed no appreciable difference between the degree of purity of the rods which had been acted on and those which had not, and an attempt to increase the action by wrapping portions of the rods with platinum foil gave entirely negative results. Some of the crystals, when dried to a constant weight in a vacuum desiccator over sulphuric acid, gave the following results on analysis:

0·2135 gave 0·121 $SnO_2$. Sn = 44·66.
0·2296 „ 0·1503 $CO_2$ and 0·036 $H_2O$. C = 17·85; H = 1·74.
$C_4H_4O_6Sn$ requires Sn = 44·57; C = 17·98; H = 1·50 per cent.

A further portion of the crystalline substance, when dissolved in dilute hydrochloric acid, produced exactly the same rotation of the plane of polarised light as a solution containing the equivalent quantities of tin and tartaric acid in the proportions necessary to form stannous tartrate. The crystals consisted therefore, as might have been expected, of stannous tartrate, a substance which, so far as I am aware, has never previously been obtained in this manner. Inasmuch as the corrosion of the rods was most marked at the surface of the liquid, it appeared very probable that oxygen was concerned in the process, and an experiment was devised to test this point. A roll of pure tin foil was partly immersed in a 5 per cent. aqueous solution of tartaric acid contained in a small glass tube, which was sealed on to a manometer, so that any absorption of the oxygen could be measured. Within a very short time of commencing the experiment the pressure began to fall, and at the end of one day it had become reduced from 929 mm. to 845 mm., and at the end of two days it had fallen to 827 mm. (a point which corresponded with the absorption of more than half the oxygen). The tin was greatly corroded at the surface of the liquid, whilst the immersed portion remained perfectly bright, and was apparently unattacked. At the same time a quantity of a white, flocculent substance separated. This entirely confirms the statements of Hall (*J. Amer. Chem. Soc.*, 1883, **4**, 440) and of Lehmann (*Arch. Hygiene*, 1907, **63**, 67), that in the absence of oxygen, tartaric acid has very little action on metallic tin. An examination of the liquids in which the tin rods had been immersed was next made. It was found that, on adding a solution of calcium chloride to the brown liquid, a buff-coloured, gelatinous precipitate was obtained, whilst no precipitate was formed in the colourless solutions. As it was thought that this might be the calcium salt of some organic acid formed by the action of the tin, a quantity was prepared, filtered, thoroughly washed with water, and dried at 100°. It was noticed that during the washing, as soon as almost the whole of the excess of calcium had been removed, the precipitate commenced to pass through the paper, giving an opalescent filtrate. The dry substance, which had a yellow colour, was found to contain 62 per cent. of tin, and to be practically free from carbon.

It was then observed that sodium chloride, sodium acetate, hydrogen chloride, and other electrolytes all produced a similar precipitate, and it became evident that the liquid consisted of a colloidal solution of some oxide of tin. A quantity of the brown solution was therefore put into a parchment thimble, which was surrounded by distilled water, the water being changed daily until the dialysate was no longer acid. This dialysate was found to contain tartaric acid, but no trace of tin. It was colourless, and remained colourless even when concentrated to a very small volume. The liquid in the thimble when evaporated to dryness left a yellowish-red, transparent mass, which was free from organic matter, and when dried at 100° contained 64·5 per cent. of tin. It was very hygroscopic, rapidly absorbing more than 10 per cent. of its weight of moisture when exposed in a dry state to the air. A weighed quantity of the substance was heated on the water-bath with a known volume of standard potassium dichromate and sulphuric acid, and at the end of two days the unreduced chromic acid was estimated. Considerably less chromic acid was used than would have been the case if the whole of the tin had been in the stannous condition, and it was clear that the substance was either a mixture of the hydrated stannous and stannic oxides or possibly contained an intermediate oxide, the lower oxide or oxides constituting at least three-fourths of the total. This substance was not soluble in water even on heating on the water-bath for some days. On evaporating the brown liquid in the dialyser, no separation or gelatinisation occurred until it was almost completely evaporated to dryness. The gelatinous matter which separated at this point was readily soluble in water, giving a clear solution, but when once it had been evaporated to dryness, the residue was completely insoluble. Although not identical in quantitative composition, it is no doubt essentially the same qualitatively as the product produced by precipitation with calcium chloride and other electrolytes. The brown liquid in the experimental bottles was found to contain 0·063 gram of tin per c.c., whilst the colourless liquid contained only 0·006 gram of tin per c.c. On passing hydrogen sulphide into the coloured solution the colour changed to a very dark brown, but no precipitation occurred. On adding a few drops of hydrochloric acid, however, a dark brown precipitate of sulphide at once formed. The addition of hydrogen sulphide to the colourless liquid from the bottles caused an immediate precipitation. In the next place, it was decided to study the behaviour of the pure crystallised stannous tartrate towards water and tartaric acid solutions. On heating stannous tartrate crystals with water, decomposition occurs, a colourless, opalescent liquid being formed, which remains opalescent even when filtered through papers of the closest texture. On passing hydrogen sulphide through this liquid, no precipitation is formed, but a deep brown liquid having a greenish fluorescence results. The liquid itself was strongly acid to litmus, and evidently consisted of tartaric acid and colloidal stannous hydroxide resulting from the hydrolytic dissociation of the tartrate. The solid stannous tartrate was next heated with 1 per cent., 2 per cent., and 5 per cent. solutions of tartaric acid. At first no action appeared to take place, and after heating on the water-bath for six hours, little more than a trace of the tartrate had dissolved. The clear, supernatant liquid gave an immediate slight brown precipitate, showing that a little tin had passed into solution, but that no colloid had formed. On continuing the heating for several days, it was observed that the tartrate dissolved slowly, and that the liquid, which was, of course, originally colourless, gradually acquired a deep brownish-yellow colour with a greenish fluorescence, and closely resembled in appearance the contents of certain of the experimental bottles. On passing hydrogen sulphide into this liquid, no precipitation occurred, but a deep brown coloration, characteristic of colloidal stannous sulphide, resulted. On continuing the heating for a further period of six days, it was noticed that the orange colour of the solution disappeared, giving place to a bluish-white, opalescent liquid. This gave no precipitate with hydrogen sulphide, but only a light yellow coloration. On the addition of a drop of hydrochloric acid, a yellow precipitate of stannic sulphide (probably with some oxide) at once formed. On heating some of the crystallised stannous tartrate with a 5 per cent. solution of tartaric acid in a sealed tube, no change was observed, although the heating was continued for several weeks.

As these experiments appeared to throw a great deal of light on the nature of the reactions occurring in the experimental bottles, it was decided to heat some of the orange-brown liquid from one of the bottles on the water-bath with free exposure to air. At first the colour deepened slightly, and then gradually became fainter, until at the end of a week a bluish-white, opalescent liquid remained, precisely similar in appearance to that obtained in the above experiment with the stannous tartrate. A small quantity of a colourless, transparent jelly separated, which doubtless consisted of the gel of colloidal hydrated stannic oxide. This liquid gave only a yellow coloration with hydrogen sulphide, but on the addition of a drop of hydrochloric acid, a copious precipitate formed. On adding a drop of hydrochloric acid to the colourless, opalescent liquid, a gelatinous precipitate formed which dissolved in an excess of the acid. The liquid evidently consisted therefore of a colloidal solution of hydrated stannic oxide, produced from the coloured solution by atmospheric oxidation. On adding a little hydrated stannous oxide to the colourless solution, the orange-brown colour returned.

In the light of the results of these experiments, I think the reactions occurring in the experimental bottles can be completely explained. Certain of the bottles had by chance (for at the time I attributed no importance to this point) been closed with well-fitting corks, and consequently the only oxygen available was that contained in the few c.c. of air above the liquid. In these, practically no action occurred, the tin remaining quite bright, or, at the most, exhibiting an etched appearance. In others, however, owing chiefly to the fact that the tin rods were not quite round, and so did not tightly close the holes bored through the corks, air could enter so soon as a reduction of pressure, due to the union of oxygen with the metal, occurred within the bottles. A very gradual supply of oxygen was thus maintained, in a manner which could not have been improved upon if the experiment had been specially devised for the purpose. It is quite clear that under the influence of the tartaric acid the tin is readily attacked by oxygen, with the formation of stannous tartrate. Under the conditions of the experiment this probably, in the course of time, forms supersaturated solutions, from which the tartrate slowly crystallises, usually on the surface of the tin, but occasionally on the surface of the glass. The tartrate so formed undergoes dissociation, and the resulting stannous hydroxide, in the presence of the very limited supply of air, undergoes slow oxidation with the formation of the coloured compound above mentioned. Owing to the fact that only a very small quantity of oxygen was able to obtain access to the contents of the bottles, and that this would have to serve the double purpose of oxidising the tin and of oxidising the stannous salt formed, this coloured compound escaped conversion into the colourless stannic compound, which would undoubtedly have taken place if there had been free access of air or less tin. Owing to the great purity of the stannous tartrate formed under these conditions—that is to say, to the absence of electrolytes—the resulting colloidal solutions exhibited a high degree of stability, and, as will be seen by reference to the numbers given above, attained a considerable strength. Incidentally, it will be seen that these results are opposed to the statement of Bouquet (*J. Pharm. Chim.*, 1847, **11**, 459), that stannous tartrate dissolves in hot water without decomposition. Several observers have called attention to the formation of a dark-coloured compound intermediate between stannous and stannic oxide, the compound having been first referred to by Frémy in 1844, who obtained a reddish-coloured powder by adding metastannic acid to a solution of stannous chloride, but, so far as I am aware, it has not been hitherto obtained by direct oxidation of the lower oxide. This coloured compound has been regarded as a compound of the two oxides, but the above mode of formation rather tends to support the view that it may be the hydrated sesquioxide, the existence of which is very probable, on theoretical grounds, and which receives further support from the fact that the existence of tin triethyl has been definitely established by Rügheimer (*Annalen*, 1908, **364**, 51). As against the view that the coloured substance is a molecular compound of stannous and stannic oxide, the following experiment may be instanced.

Solutions were prepared containing stannous sulphate, ammonium persulphate, and quantities of sulphuric acid, varying from 1 to 20 per cent. These solutions were allowed to remain, and at the end of some weeks it was found that in all cases a certain amount of colour had developed, the colour being deepest in the solutions containing the largest proportions of sulphuric acid. Under these conditions it is almost inconceivable that any compound, such as stannous stannate, should be capable of existing. Attempts have been made to isolate the intermediate oxide and to prepare salts corresponding with it, but up to the present without success. This work is being continued. Mr. Emil Hatschek, who has been kind enough to examine the coloured colloidal solution ultra-microscopically, reports as follows:

"For the purpose of ultra-microscopic examination, the solution was diluted to fifty times its volume, and the dilute solution was examined with the Jentzsch and the Reichert ultra-condensers. On diluting the solution with tap water, it became turbid, and showed an enormous number of submicrons. The solution accordingly appears to undergo coagulation by the small amount of electrolytes present in tap water, and thus exhibits a sensitiveness not usually found in the classical stannic acid solutions, but characteristic of certain solutions of aluminium hydroxide.

"If distilled water is used, the dilute solution is perfectly clear and stable. In the ultra-microscope it shows a small number of particles, probably due to incipient coagulation by carbon dioxide contained in the distilled water. The solution, like the known solutions of stannic acid and practically all solutions of metallic hydroxides, is therefore also an emulsoid solution."

My best thanks are due to my assistant, Dr. E. Wechsler, for valuable assistance in connexion with this work.

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## LXXIX.—*Some Double Salts with Acetone of Crystallisation and the Crystallisation of Silver Iodide, Silver Bromide, and Cuprous Iodide.*

By JAMES ERNEST MARSH and WILLIAM CLAUDE RHYMES.

IN 1910 (T., **97**, 2297) some liquid ether compounds of double halogen salts were described, which were chiefly mercury compounds, but silver iodide, cuprous iodide, and lead iodide were found to give liquid compounds with lithium iodide and ether. In the present paper a complete series of crystalline double salts of silver iodide with the alkali-metal iodides is described. These salts are of the type MI,2AgI. Evidence is also given of the existence of salts of the type MI,3AgI, and of salts containing less than 2AgI.

We have also made, but have not completed the examination of, a series of double cuprous iodides. It was found that when the ethereal solution of lithium silver iodide (*loc. cit.*, p. 2308) was allowed to evaporate, crystals of silver iodide were deposited, and that these crystals, together with the deliquesced lithium iodide, were soluble in acetone, and crystallised out again on evaporation of the acetone. In a similar way, silver bromide and cuprous iodide have also been obtained in the crystalline state.

The salts described in this paper were obtained by crystallisation from acetone, and most of them contain acetone of crystallisation. They lose this acetone with great rapidity on exposure to the air, and either effloresce and crumble to powder or deliquesce. The determination of the acetone of crystallisation thus presented considerable difficulty. The method which was in general adopted is as follows: The double salt with some excess of solvent was contained in a Liebig drying tube; a current of dry air was passed through the tube until the excess of solvent was removed; acetone vapour was then passed through the tube until the crystals began to liquefy; then dry air was passed until the crystals were just dry. The method, perhaps, does not lend itself to extreme accuracy, but it gave fairly consistent results. The lithium, sodium, ammonium, and potassium double silver salts deliquesce in contact with acetone vapour under these conditions; the rubidium and cæsium salts do not.

### *Caesium Silver Iodide*, CsI,2AgI.

This is the only salt of the series which does not take up acetone of crystallisation. It is more soluble in cold than in hot solution, differing in this also from the other salts. It is also much the least soluble. It was obtained by dissolving a mixture of cæsium and silver iodides in the molecular proportion of 1 to 2 in 20 to 30 times its weight of acetone cooled with ice and salt. The solution was filtered from a little sediment, and crystallised by evaporation of the acetone. If the solution is warmed, the salt is precipitated, but not in good crystals. On evaporation the salt separates in long, hair-like crystals, which are colourless and double refracting with straight extinction. They remain colourless up to their melting point at about 210°. The fusion is yellow, and quickly separates a yellow solid, probably silver iodide. The crystals are free from acetone, and are stable in the air. They do not absorb acetone or water vapour, but when placed in water decompose with separation of silver iodide. The crystals lost less than 0·3 per cent. of their weight on heating, and were therefore free from acetone and water.

Found, AgI = 63·9.

CsI,2AgI requires AgI = 64·4 per cent.

### *Rubidium Silver Iodide*, $RbI,2AgI,2C_3H_6O$.

This salt is obtained when rubidium iodide and silver iodide are dissolved in acetone, and the solution evaporated in dry air.

It is extremely soluble in the solvent, and a hot, strong, saturated solution crystallises on cooling. The crystals were obtained in transparent, colourless needles, double refracting, with straight extinction; on exposure to the air they lose their acetone and crumble to powder. The dry salt does not deliquesce, but absorbs water slightly from the air:

Found, $C_3H_6O = 14{\cdot}8$.

$RbI,2AgI,2C_3H_6O$ requires $C_3H_6O = 14{\cdot}5$ per cent.

Found (in dried salt) $AgI = 68{\cdot}67$.

$RbI, 2AgI$ requires $AgI = 68{\cdot}9$ per cent.

Rubidium iodide does not appear to form a double salt with silver iodide in equal molecular proportions, or, at any rate, the compound $RbI,AgI$ * is not soluble in acetone at the ordinary temperature. Some of the rubidium iodide is left undissolved. More of it, however, is dissolved than corresponds with the formula $RbI,2AgI$. Since rubidium iodide and silver iodide separately are scarcely at all soluble in acetone, another double salt, containing a larger amount of rubidium iodide, is perhaps indicated possibly $2RbI,3AgI$. A salt with excess of silver iodide, of the formula $RbI,3AgI$, is also indicated, but has not been analysed. It was noticed, when dissolving the salts in the proportion 1 : 2, that the silver iodide dissolved before the rubidium iodide, and on addition of another molecular proportion of silver iodide it dissolved when the liquid was cooled. A little below 0°, the whole solution froze to a hard, solid mass.

### *Potassium Silver Iodide*, $KI,2AgI,2C_3H_6O$.

The potassium salt was obtained in the same way as the rubidium salt, and gave crystals closely resembling the latter in appearance:

Found, $C_3H_6O = 16{\cdot}36$.

$KI,2AgI,2C_3H_6O$ requires $C_3H_6O = 15{\cdot}4$ per cent.

The result is perhaps as accurate as one could expect from the slight hold the salt has on its acetone of crystallisation:

Found (in dried salt), $KI = 25{\cdot}5$.

$KI,2AgI$ requires $KI = 26{\cdot}1$ per cent.

The salt on exposure to the air loses its transparency with loss of acetone. The acetone-free salt takes up water from the air without deliquescing. Like the rubidium salt, a solution can be obtained in acetone of potassium and silver iodides in the proportion of KI to 3AgI. In a freezing mixture of ice and salt, the solution, if not too diluted, freezes to a solid mass. When warmed, the solution deposits some of the silver iodide in the amorphous form.

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* The salt $RbIAgI,\frac{1}{2}H_2O$ has since been obtained by crystallisation from a mixture of acetone and water.

Potassium and silver iodides dissolve in acetone also in the proportion of KI to AgI. On evaporation of the acetone, crystals are left which deliquesce in moist air, forming a solution from which crystals of silver iodide eventually separate. Potassium silver iodide, KI,2AgI, is soluble in other ketones, such as methyl ethyl ketone, which gives a solution of a deep orange colour. Diethyl ketone also dissolves it, but not quite completely, and possibly some decomposition occurs. The solution in diethyl ketone, like that in acetone, is nearly colourless.

### *Sodium Silver Iodide*, $NaI,2AgI,3C_3H_6O$.

This salt forms colourless, transparent, needle-shaped crystals, double refracting, with straight extinction.

It is extremely soluble in acetone, and on evaporation of the acetone a jelly-like mass is left, in which the crystals gradually form:

Found, $C_3H_6O = 21{\cdot}59$.

$NaI,2AgI,3C_3H_6O$ requires $C_3H_6O = 21{\cdot}91$ per cent.

Found (in dried salt), $AgI = 76{\cdot}1$.

$NaI,2AgI$ requires $AgI = 75{\cdot}8$ per cent.

Sodium and silver iodides dissolve in acetone in equal molecular proportions, but the crystals on evaporation do not appear to be homogeneous. Nor has the phenomenon of solution in these proportions the same significance as the solution of the salt KI,AgI, since sodium iodide by itself is readily soluble in acetone.

### *Lithium Silver Iodide.*

This salt crystallised well from dry acetone in colourless needles, with strong double refraction and straight extinction.

The determination of the acetone of crystallisation did not give very concordant results, the amount varying between three and four molecules. The salt does not crystallise out at all when the solution is allowed to evaporate exposed to the air. The crystals are obtained by evaporating the acetone in a current of dry air. When the acetone solution is exposed to the atmosphere crystals of silver iodide are gradually formed. This phenomenon is referred to again later.

### *Ammonium Silver Iodide*, $NH_4I,2AgI,3C_3H_6O$.

This salt crystallises well from acetone in colourless needles, double refracting, with straight extinction. We have not at present sufficient crystallographic evidence to determine whether the crystalline form of this salt is different from that of the potassium salt.

Found, $C_3H_6O = 21{\cdot}8$.

$NH_4I,2AgI,3C_3H_6O$ requires $C_3H_6O = 22{\cdot}0$ per cent.

Found (in dried salt), $AgI = 77{\cdot}0$.

$NH_4I,2AgI$ requires $AgI = 76{\cdot}4$ per cent.

An ethylamine hydriodide–silver iodide was also crystallised from acetone, and resembled the ammonium salt in general appearance. There seems to be no doubt that a whole series of organic compounds of this type are capable of existing.

### *Crystallised Silver Iodide.*

When a solution of silver iodide in lithium iodide and acetone is exposed to the air, after some days crystals of silver iodide begin to form and grow in the solution. The crystals are of the hexagonal form and transparent, and there seems to be no difficulty in obtaining crystals in this way of any desired size. Silver chloride also dissolves in an acetone solution of lithium iodide, and silver iodide crystallises from the solution. These crystals were analysed by conversion into silver chloride in a current of chlorine. As the iodine is displaced by the chlorine, the crystals crumble to powder without heat being applied to them:

0·6120 gave 0·3716 AgCl. $Ag = 45{\cdot}7$.

AgI requires $Ag = 45{\cdot}9$ per cent.

### *Crystallised Silver Bromide.*

Lithium bromide and silver bromide dissolve fairly well in acetone, in the proportions of LiBr to 2AgBr. Like cæsium silver iodide, the solubility is greatest in the cold solution. As the temperature is allowed to rise, silver bromide crystallises out in large, flat, yellow, transparent plates, which are very tough and flexible. To obtain good crystals, the acetone should be pure, that obtained from bisulphite being the best. The crystals lost 1·22 per cent. of their weight on heating, which is probably due to included solvent:

1·0269 gave 0·7718 AgCl. $Ag = 57{\cdot}2$.*

AgBr requires $Ag = 57{\cdot}4$ per cent.

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* Allowance is made for 1·22 per cent. of volatile impurity.

### *Double Cuprous Salts and Crystalline Cuprous Iodide.*

Cuprous iodide is readily soluble in acetone in the presence of an alkali-metal iodide. Sodium iodide and cuprous iodide dissolve in acetone in the proportions of NaI to 2CuI. On evaporation, a well-crystallised salt is obtained. Lithium iodide and cuprous iodide also dissolve in acetone in about the same relative proportions. On slow evaporation in the air cuprous iodide crystallised out. The crystals are fairly large and colourless, but opaque.

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## LXXX.—*Notes on the Determination of the Electrical Conductivity of Solutions.*

By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

IN a series of experiments preliminary to the determination of the temperature-coefficients of the electrical conductivity of dilute salt solutions, the resistance of a solution was measured both with a commutator of the pattern described by Whetham (*Phil. Trans.*, 1900, *A*, **194**, 321) and with a telephone and induction coil. As the latter method appeared to give a lower value for the resistance, a careful comparison of the two methods has been made. The results show that they do not yield the same value for the resistance, and that the ratio of the resistances found by them varies (1) with the construction of the commutator, (2) with the rate at which the commutator is driven, (3) with the magnitude of the resistance to be measured, (4) with the form of the cell.

In the course of the work a new form of conductivity cell was devised for use with dilute solutions, which possessed several advantages over the usual patterns, and has since been found most useful in the investigation of both aqueous and non-aqueous solutions.

### *Comparison of the Values found for the Electrical Resistance of a Solution by the Commutator and Telephone Methods.*

The resistance of solutions of potassium chloride (approx. 0·001*N*) was measured between three pairs of platinum plates: (*a*) a pair of small plates (area 2·5 sq. cm.) coated with platinum black, and placed close together in a cell of the Arrhenius pattern; and (*b*) and (*c*) two separate pairs of platinum plates of a larger size (area 6 sq. cm.) coated with grey platinum obtained by heating platinum black to dull redness (Whetham, *loc. cit.*, p. 329) in a large cell containing 1500 c.c. of solution. The solutions being so dilute, special precautions were taken to protect them from contamination with impurities during the measurements, and the resistance of the solutions was tested at the end of each experiment by the method in use at the beginning, in order to see that it had not varied.

In the first set of experiments the results obtained with a double pole Bell telephone of the ordinary pattern and a small induction coil were compared with those obtained with a rotating commutator with eight sectors and insulated strips separating each pair. The commutator was driven by a small motor, and the speed was altered by varying the resistance in the motor circuit. A Nalder galvanometer was used as a current detector. The bridge consisted of three metres of wire wound on a marble drum, with extensions which increased its effective length to 30 metres. An accumulator was used as the source of current with the rotating commutator, a resistance of 2000 ohms being placed in the battery circuit.

TABLE I.

*Resistances in Ohms.*

| | | By commutator. | | | |
|---|---|---|---|---|---|
| Electrodes. | By telephone. | High speed. | Low speed. | | |
| | $r_1$. | $r_2$. | $r_3$. | $r_2/r_1$. | $r_3/r_1$. |
| *A.* Black Pt ... | 237·51 | 238·77 | 238·60 | 1·0053 | 1·0046 |
| *B.* Grey Pt ... | 1391·6 | 1401·2 | 1399·4 | 1·0069 | 1·0056 |
| *C.* ,, Pt ... | 2264·7 | 2277·6 | 2274·3 | 1·0057 | 1·0042 |

These results show that the telephone gives a lower value for the resistance than the commutator, and that the value of the resistance found by the latter depends to a small extent on the rate at which the commutator is driven. An increase of speed, that is, an increase in the number of alternations per minute and a decrease in the length of time during which a direct current flows through the solution, leads to a lower value for the resistance.

In some further experiments, in which the largest resistance measured was 2200 ohms, it was found (1) that if the electrolytic resistance is measured by a telephone and induction coil, the result is independent of the note the telephone is giving, and does not vary with different telephones and coils, and (2) that if two wire resistances not exceeding 4000 ohms are compared with a rotating commutator, the result is independent of the rate at which the commutator is driven, and is identical with the result obtained with a telephone.

A further comparison was made with the same pairs of electrodes in solutions of potassium chloride of nearly the same strength by three independent observers (Mr. T. S. Moore and the authors), in order to eliminate the effect of personal error; individual results never differed from one another by more than five parts in ten thousand, and usually agreed more closely. To increase the value of the comparison, a different pattern of commutator, kindly lent by Mr. B. Lambert, was also used. It was made with only two sectors. The number of alternations was determined by means of a revolution counter. The resistance in the battery circuit in all the commutator measurements was 700 ohms. The results are given in the following tables:

### TABLE II.

*Resistances in Ohms.*

| | By telephone, | By commutator (two sectors). | | By commutator (eight sectors). | | | |
|---|---|---|---|---|---|---|---|
| | | 2200 alts. | 2750 alts. | 2640 alts. | 3200 alts. | 5700 alts. | 6500 alts. |
| | $r_1$. | $r_2$. | $r_3$. | $r_4$. | $r_5$. | $r_6$. | $r_7$. |
| *A.* | 236·94 | 238·65 | 238·69 | 238·24 | — | — | 237·74 |
| *B.* | 1388·6 | 1400·6 | 1399·0 | 1395·6 | 1394·8 | 1394·0 | 1392·2 |
| *C.* | 2260·9 | 2277·5 | 2275·6 | 2271·4 | — | — | 2266·2 |

*Ratios of Resistances Determined by Telephone and Commutator.*

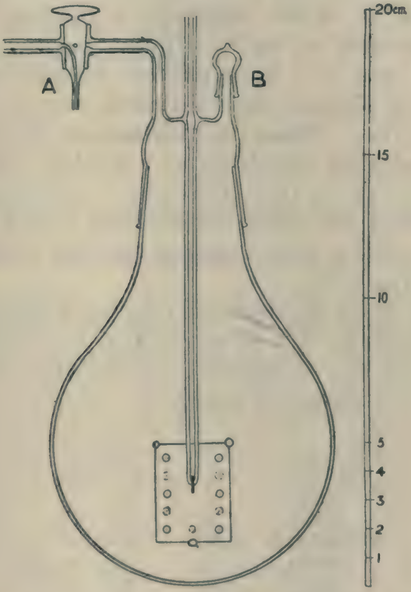
| | $r_2/r_1$. | $r_3/r_1$. | $r_4/r_1$. | $r_5/r_1$. | $r_6/r_1$. | $r_7/r_1$. |
|---|---|---|---|---|---|---|
| *A.* | 1·0072 | 1·0074 | 1·0055 | — | — | 1·0034 |
| *B.* | 1·0086 | 1·0075 | 1·0050 | 1·0045 | 1·0039 | 1·0026 |
| *C.* | 1·0073 | 1·0065 | 1·0046 | — | — | 1·0023 |

These results agree with those obtained in the preliminary series. Using the eight-sector commutator at 2600 revolutions per minute, the resistance with each kind of plate is, roughly, 0·5 per cent. higher than that found with the telephone. As the number of revolutions increases, the resistance appears to diminish, and its value approaches that found with the telephone. The higher the resistance the more closely does the resistance measured by the commutator agree with that found by the telephone. However, in some later experiments with Mr. Bourdillon, when higher electrolytic resistances (up to 250,000 ohms) were measured by both methods, large differences, amounting in some cases to 5 per cent., were observed.

### *Conductivity Cell for Use with Dilute Solutions.*

In order to determine the conductivity of aqueous solutions more dilute than 0·001*N*, when the conductivity of the solvent under the best conditions amounts to 1 or 2 per cent. of the conductivity of the whole solution, it is necessary to start with a considerable quantity of the solvent (compare Whetham, *loc. cit.*; Kohlrausch and Maltby, *Wiss. Abh. Phys. Tech. Reichsanstalt*, **3**, 157) in a cell which protects it from contamination with the air, and to add to it from weight- or volume-pipettes successive small quantities of a solution of the electrolyte under examination.

It must be possible to make these additions and to stir the contents of the cell without any risk of introducing impurities from the air. These conditions are fulfilled by the cell shown in the figure. It is made entirely of boro-silicate glass, and holds about 300 c.c. of solution. The tubes carrying the platinum are fused through the cap of the cell, and the electrodes are held firmly together by small rods of glass fused on at the corners. They are covered with grey platinum (obtained by heating platinum black to redness) to avoid occlusion by platinum black (compare Whetham, *loc. cit.*, p. 329). The water or solution can be stirred by rotating the cap of the cell; the holes in the electrodes shown in the figure ensure the stirring of the solution between the plates even when they are within a few mm. of one another. The tap *A* admits a current of air freed from carbon dioxide and ammonia by passing through sulphuric acid and over soda-lime, and then through water to saturate it with water vapour.



At the beginning of an experiment the cell is cleaned with conductivity water and dried, and a current of purified air passed through for some minutes. It is then weighed, and conductivity water is run in through the opening *B* until the surface reaches an etched mark on the cell. The mark is placed at such a height above the electrodes that the cell constant does not vary when small quantities of solution are added to the solvent. The cell is then weighed again to ascertain the weight of water it contains, and put into the thermostat. The water is stirred, and its resistance measured from time to time. Any change in the resistance that may have taken place after the temperature of the water has reached the temperature of the bath is due either to the solubility of the glass, to the solution of electrolytes absorbed by the electrodes, or to the exchange of volatile impurities with the air in contact with the water. If the resistance is falling, it is a good plan to pass in a little purified air, the cap at *B* being removed for a few seconds; this will often stop the fall and cause the resistance to rise. When the resistance of the solvent water is steady, small measured quantities of a solution of the electrolyte to be studied are run in from a weight- or volume-pipette, a slow current of purified air being admitted at *A* so as to prevent atmospheric impurities from entering the cell while the addition of solution is being made.

The following series of measurements show that the constancy of the solvent resistance can be maintained for a considerable time with water which has a specific conductivity of approximately 1 gemmho ($1 \times 10^{-6}$ reciprocal ohms).

| Time, hrs. | mins. | Resistance, in ohms. |
|---|---|---|
| — | — | 30400 |
| — | 20 | 30500 |
| — | 22 | 30500 X |
| — | 25 | 30500 |
| — | 28 | 30600 |
| — | 30 | 30600 |
| 19 | — | 30800 |
| 19 | 30 | 30800 X |
| 20 | — | 30900 |
| 21 | — | 30900 X |
| 22 | — | 30900 X |
| 23 | — | 30800 |

At points marked X the cap *B* was removed, and a slow current of air admitted at *A*, in order to show that portions of solution could be added without changing the resistance of the solvent.

Using water with a conductivity as low as 0·11 gemmho, Mr. Bourdillon found that the average rise per hour was 0·004 gemmho when the electrodes had not been in contact with a salt solution for some time, and 0·01 gemmho when they had been soaked for twelve hours in pure water after use with 0·05*N*-solution of potassium chloride.

In order to allow the cap of the cell to rotate easily and to ensure good stirring, the ground joint is lubricated with a little vaseline previously purified by being heated with conductivity water to remove traces of organic acids. Care must be taken always to set the cap of the cell in the same position; for this purpose marks are etched on the edge of the cap and on the neck of the flask, and these are brought into coincidence. Since the cap is ground on outside the neck of the flask, there is no fear of dust falling in while the cap is being rotated.

The authors have pleasure in acknowledging their indebtedness to a grant from the Research Fund of the Royal Society, from which much of the cost of the apparatus used in this work was defrayed.

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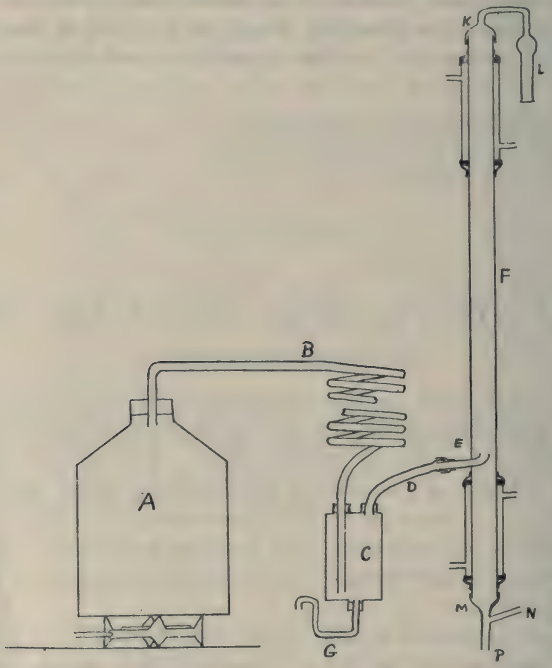
# LXXXI.—*The Preparation of Conductivity Water.*

By ROBERT BOURDILLON.

HITHERTO most work on the conductivity of dilute solutions has been done with water possessing an electrical conductivity of at least 0·7 gemmho ($0·7 \times 10^{-6}$ reciprocal ohms). The use of such water involves a correction for solvent conductivity which may amount to 8 per cent. or more in $N/10,000$-solution; since this correction is uncertain for salt solutions, and leads to most anomalous results for solutions of dilute acids, it is obviously important to reduce it as far as possible.

This paper describes a still which will deliver 7 or 8 litres of water of conductivity below 0·2 gemmho in a single distillation from Oxford tap water. It is also found that in a suitable air-tight cell such water can be kept with only a very slow rise in conductivity.

The boiler *A* (see diagram) is of copper and holds about 13 litres. It is closed by a rubber cork, through which passes a copper tube *B* (1·3 cm. external diameter, 8·5 metres long) coiled into a spiral of 19 turns. This spiral forms an efficient trap for spray, and its lower end is fixed by a rubber cork into a copper cylinder *C*. *B* and *C* are jacketed with cotton waste and boiler felt, but about one-fifth of the steam from the boiler is condensed here; this waste water escapes by the glass tube *G*, which is joined to *C* by a rubber cork, and bent as shown in the diagram in order to prevent the escape of steam. The steam passing through *B* and *C* goes up the glass tube *D** into the condenser at *E*. The condenser is a long, vertical tin tube *F* (2·5 cm. internal diameter, 145 cm. long), with a narrow side-tube *E* soldered in with pure tin 45 cm. from the bottom, and turned upwards inside *F*. *F* is surrounded near the top and bottom by glass tubes through which cold water is passed, and is closed at the top by a glass cap *K*, which is affixed by a rubber ring and is connected with the air by a soda-lime tube *L*, and at the bottom by a glass cap *M*, carrying a side-tube *N*, and joined by rubber tubing at *P* to the vessel in which the distilled water is to be collected. *K* and *M* might with advantage be made of tin, and soldered to *F* with tin. A continuous current of purified air (usually 3—3·5 litres per hour) enters at *N*, and passes out at *L*. It is purified by passing through glass spirals containing concentrated sulphuric acid and potassium hydroxide solution, and then through a long soda-lime tube. The continuous current of air was obtained by allowing a slow stream of water to fall down a vertical glass tube after the manner of a Sprengel pump; the tube



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* The tube *D* is joined to *C* by a rubber cork, and to *E* by a short piece of rubber tube; it is unnecessary, and is included in the author's still only because of the position in the laboratory in which the still is placed. It would be better to attach *E* directly to *C*.

was connected at the bottom to a large bottle, from which the water and air were allowed to escape by separate outlets.

The boiler is filled with tap water, to which about 5 grams of potassium hydrogen sulphate have been added. When boiling begins, the greater part of the carbon dioxide is expelled rapidly, and the ammonia is retained. The steam passes through *B* and *C*, and leaves the tube *E* with a considerable upward velocity (as may be seen by removing the cap *K*). On reaching the part of *F* which is surrounded by the top cooling tube, it condenses, and the water thus formed trickles down past a long column of steam and purified air, which apparently removes the volatile impurities. The object of the lower cooling tube is to cool this water to any desired temperature before it leaves the condenser, and very little water is condensed here.* It is most important to keep all connexions air-tight; the work was done in a cellar without good ventilation, and it was found that any leak in the apparatus produced a large rise in the conductivity of the water.

If the distillation is carried on fairly fast (1·2 litres per hour), the conductivity of the resulting water falls rapidly, and remains below 0·13 gemmho after one litre has been collected. It is found advisable to stop the distillation when two or three litres are left in the boiler, in order to prevent incrustation from calcium sulphate. The following table shows the average course of a distillation, and was obtained by attaching a conductivity cell directly to the condenser.

| Time in minutes from beginning of distillation. | Conductivity in gemmhos at 18°. | Total volume of distillate in c.c. |
|---|---|---|
| 7 | 4·2 | 100 |
| 10 | 1·4 | 170 |
| 13 | 0·91 | 240 |
| 15 | 0·48 | 310 |
| 18 | 0·25 | 385 |
| 21 | 0·15 | 460 |
| 24 | 0·14 | 530 |
| 27 | 0·11 | 600 |
| 30 | 0·11 | 670 |
| 4 hrs. 15 mins. | 0·11 | about 6000 |

From the first half hour until the distillation is stopped, the values found vary from 0·11 to below 0·09 gemmho, occasionally rising to 0·12.

The values given above are only approximate, and may contain an error of 10 per cent., but they are confirmed by a number of observations made with the cell described below. The lowest value observed in this cell was 0·086 gemmho at 18°, but there are indications that the conductivity of the water at the mouth of the condenser falls below this. The lowest value obtained by Kohlrausch and Heydweiller by distillation in a vacuum was 0·04 gemmho at 18°.

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* The top cooling tube needs a rapid stream of cold water, the bottom tube needs much less; in order to cool the distilled water to any desired temperature, it is best to connect the two tubes to separate water taps.

If phosphoric acid is used in the boiler instead of potassium hydrogen sulphate, very similar results are obtained. If no chemicals are used, a large quantity of mediocre water is obtained, the conductivity falling to 0·3 gemmho about two hours after distillation begins, and only falling to 0·17 gemmho after 4·5 hours' distillation. If distilled water is used instead of tap water and potassium hydrogen sulphate is added, slightly better water is obtained, but there is little difference, and the conductivity of the product does not fall much below 0·09 gemmho. If tap water is distilled with potassium hydrogen sulphate but no pure air is passed up the condenser, the conductivity of the product falls to about 0·25 gemmho after some hours, but does not fall below this value. A few trials were made with a condenser similar in form to that described above, but only 46 cm. long and 2 cm. internal diameter, but no water was obtained of a conductivity of less than 0·23 gemmho.

*Behaviour in Conductivity Cell.*—Nothing is gained by using such water in a conductivity cell that is not air-tight. Hartley and Barrett (this vol., p. 788) have devised a cell which is very convenient, as its contents can be stirred and fresh solution can be added without risk of contamination from the air. It is made of borosilicate glass, and if its electrodes have been soaked in water for a long time, and it is then filled with purified air, water with a conductivity of 0·11 gemmho increases its conductivity by about 0·02 gemmho during the first hour after it is placed in the cell, and during the second and subsequent hours the rise is only 0·004 or 0·003 gemmho per hour. If the cell has contained $N/20$-potassium chloride solution, and has then been thoroughly washed and left to soak for one night with pure water in it, the rise during the first hour is about 0·03 gemmho, and that during the next few hours is about 0·01 gemmho per hour. An alteration of 0·05 gemmho in the conductivity of the solvent would change the apparent conductivity of $N/10,000$-potassium chloride solution by about 0·05 per cent. Since it is easy to take measurements of a solution within half an hour of the determination of its solvent conductivity, it is evident that the alteration in the solvent is so small that a correction for it can be made safely, even in very accurate work.

As yet only a few attempts have been made to keep water of low conductivity for any length of time. It was found that, on collecting and storing water in 3-litre Jena-glass flasks fitted with siphon outlet tubes, and with air inlets protected by soda-lime tubes, the conductivity rose from 0·12 gemmho, when first collected, to 0·2 gemmho in two or three days, and to 0·4 or 0·45 gemmho in two or three weeks. It can be kept for a month or two without its conductivity rising above 0·5 gemmho.

In conclusion I should like to express my thanks to Mr. Hartley for much valuable advice and help. The cost of the measuring apparatus used in this research was defrayed by a grant from the Government Grant Committee of the Royal Society, made to Mr. Hartley for the investigation of the conductivity of dilute aqueous solutions.

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# LXXXII.—*The Reaction between Ferric Salts and Thiocyanates.*

By JAMES CHARLES PHILIP and ARTHUR BRAMLEY.

THIS reaction has been the subject of numerous investigations, many of them carried out with the object of applying the law of mass action to the equilibrium which is established between the various substances concerned, and which is generally represented as follows:

$$FeCl_3 + 3KCNS \rightleftarrows Fe(CNS)_3 + 3KCl.$$

The displacement of equilibrium which results from change of concentration or temperature has been deduced from the corresponding changes in the colour intensity (see Gladstone, *Phil. Trans.*, 1855, **145**, 179; Krüss and Moraht, *Annalen*, 1890, **260**, 193; Magnanini, *Zeitsch. physikal. Chem.*, 1891, **8**, 1; Vernon, *Chem. News*, 1892, **66**, 177, 191, 202, 214; 1893, **67**, 66; Gladstone, *ibid.*, 1893, **67**, 1; Rosenheim and Cohn, *Zeitsch. anorg. Chem.*, 1901, **27**, 280).

There is, however, one fact which has a very definite bearing on the relation between ferric salts and thiocyanates, and to which too little attention has been paid, although it has been observed by a number of workers. This fact is the gradual diminution in the intensity of colour which takes place in a given solution of ferric thiocyanate (see, for instance, Vernon, *loc. cit.*; Oerum, *Zeitsch. anal. Chem.*, 1904, **43**, 152; Stokes and Cain, *J. Amer.*

*Chem. Soc.*, 1907, **29**, 412, 445). It has been noted by some investigators that this bleaching is associated with a reduction of the iron from the ferric to the ferrous condition (Stokes and Cain, *loc. cit.*, 412; compare Rosenheim and Cohn, *loc. cit.*; Tarugi, *Gazzetta*, 1904, **34**, ii, 326; Bongiovanni, *ibid.*, 1907, **37**, i, 472), but apparently there are no definite recorded data bearing either on the nature of the corresponding oxidation products, or on the velocity of the reduction and its variation with concentration, temperature, acidity, etc.

The fact that there is a progressive reduction of the iron in a ferric thiocyanate solution was discovered incidentally in the course of another investigation, and independently of the observations recorded by previous workers. It was then thought worth while to search for the oxidation products which must necessarily be formed in proportion as the iron is reduced.

Judging from the recorded action of common oxidising agents on thiocyanic acid, the authors expected to find that at least the main oxidation products would be hydrocyanic and sulphuric acids. Investigation showed, however, that at the ordinary temperature the carbon of the thiocyanate, so far as oxidation of this substance has taken place, appears, not as cyanide, but as carbon dioxide, whilst the corresponding sulphur is converted into sulphate. Quantitative comparison of the iron reduced on the one hand, and the carbon dioxide and sulphate formed on the other, has shown that for every 8 gram-atoms of iron reduced there are formed 1 gram-molecule of carbon dioxide and 1 gram-molecule of sulphuric acid. On the basis of these facts, the decomposition of ferric thiocyanate might be represented by the equation:

$$8Fe(CNS)_3 + 6H_2O = 8Fe(CNS)_2 + 7HCNS + CO_2 + \underbrace{H_2SO_4 + NH_3}.$$

This equation, however, whilst consistent with the facts, so far as the formation of carbon dioxide and sulphuric acid is concerned, requires the production of ammonia to an extent beyond what is actually found. The quantity of ammonia obtainable from the reaction mixture is never more than about two-thirds of that required by the foregoing equation. The nitrogen therefore of the oxidised thiocyanate appears only partly as ammonia, and no definite information has been obtained as to the other product or products into which this element is converted.

The velocity of the reaction between ferric salts and thiocyanates presents various interesting features, although it has not been found possible to represent the course of the change by a mathematical formula. The study of mixtures containing a constant quantity of ferric salt and varying quantities of thiocyanate has shown that, whilst at the start the reduction is slowest in those solutions with the least thiocyanate, it proceeds at a more even rate, until ultimately the extent of reduction is greatest in these cases. This peculiar behaviour is probably connected with the influence of acid, which retards the reduction where there is excess of thiocyanate, and slightly accelerates it where there is excess of iron. This observation is significant, since the progress of the reduction means the accumulation of acid and an increase in the relative concentration of thiocyanate.

## EXPERIMENTAL.

### *The Products of the Interaction of Ferric Salts and Thiocyanates.*

The fact that in a solution of ferric thiocyanate there is a gradual reduction of the iron was discovered incidentally in the process of standardising a solution of titanium trichloride. According to the method of standardisation proposed by Knecht and Hibbert, a solution containing a known amount of iron in the ferric condition, together with some mineral acid, is employed. A large excess of potassium thiocyanate is added as indicator, and the titanium trichloride is then run in until the red coloration due to ferric thiocyanate disappears entirely. In one standardisation portions of a prepared iron solution, with the added thiocyanate, had been heated before titration, and it was found that in these cases the volumes of titanium trichloride required varied in a very marked and irregular manner. Further examination showed that extensive reduction of the iron had taken place under the foregoing conditions. It was also observed that the iron was reduced to an appreciable, if much smaller, extent, even at the ordinary temperature, when the solutions containing ferric thiocyanate were allowed to remain some time before titration. For example, 10 c.c. of a solution containing about 6 grams of iron and 80 grams of ammonium thiocyanate per litre (that is, $Fe : NH_4CNS = 1 : 9$) required, when freshly prepared, 22·7 c.c. of the standard titanium solution. One hour later, 10 c.c. of the same mixture, which had been kept at 25°, required 20·4 c.c. of the titanium chloride solution. Hence about 10 per cent. of the iron had been reduced in this interval.

That a solution containing ferric thiocyanate undergoes a gradual change with time is clearly shown by the regular increase in the electrical conductivity of the solution. Such an increase was observed for a mixture of ferric ammonia alum and potassium thiocyanate, but was especially evident when the initial solution contained nothing but ferric thiocyanate. This was prepared by treating excess of freshly precipitated and well-washed ferric hydroxide with a solution of thiocyanic acid. Table I contains a record of the relative values of the conductance ($C$) at 25° of a ferric thiocyanate solution containing 9·6 grams of iron per litre.

TABLE I.

| Time in hours. | Conductance $C$. | Time in hours. | Conductance $C$. |
|---|---|---|---|
| 0·0 | 6·60 | 136·5 | 10·78 |
| 17·5 | 8·68 | 220·0 | 11·23 |
| 41·0 | 9·61 | 449·5 | 11·71 |
| 88·0 | 10·34 | | |

This marked increase in conductivity is to be attributed to the production of new molecules, some of which at least must be largely ionised or yield ions of high mobility.

Obviously, in so far as the iron in ferric thiocyanate is reduced, there must be a corresponding oxidation of the thiocyanate. From analogy to what occurs when thiocyanates are treated with potassium permanganate, hydrogen peroxide, iodine, and hypochlorite, it was at first thought probable that the oxidation of the thiocyanate by ferric salt would lead to the formation of cyanide and sulphate. Many experiments, however, carried out with the object of detecting cyanide as one of the products of oxidation indicated that at the ordinary temperature cyanide was not formed to more than a very small extent, although at higher temperatures considerable quantities were produced. It was finally found, as already indicated, that the sulphur of the thiocyanate is oxidised to sulphate, and the carbon almost exclusively to carbon dioxide.

This result was established by the following quantitative experiments. A measured quantity of ferric salt solution of known strength was placed in a flask provided with a three-holed rubber stopper. Through two of these holes there passed glass tubes, one of which dipped into the solution and served for the admission of a current of nitrogen or air, free from carbon dioxide; the gas, after bubbling through the solution, passed on through the second tube referred to above. Through the third hole in the stopper there passed the stem of a dropping funnel, from which a measured quantity of potassium thiocyanate solution, of known strength, could be delivered. The current of nitrogen, after leaving the reaction vessel, passed in succession through (*a*) a solution of silver nitrate acidified with nitric acid, (*b*) distilled water, (*c*) a series of flasks containing measured quantities of standard baryta solution. The train of flasks was filled with nitrogen before the introduction of the baryta and the addition of the potassium thiocyanate solution to the ferric salt solution.

The experiment was started by running the potassium thiocyanate solution into the ferric salt solution, and very shortly thereafter the formation of a white precipitate in the first baryta flask was observed. At the ordinary temperature the reaction was allowed to proceed for several days, after which, as shown by experiments described later, the change becomes very slow. By this time, a large quantity of precipitate had collected in the baryta flasks, whilst there was only a slight white deposit in the silver nitrate flask, and the distilled water was neutral. The amount of carbon dioxide produced in the reaction was ascertained by determining the excess of baryta with oxalic acid solution.* The precipitate which had been formed in the baryta flasks during the experiment was examined and found to consist of carbonate; there was no sulphide or cyanide either in the precipitate or in the solution.

The examination of the reaction mixture itself consisted in the determination of (*a*) the iron reduced, (*b*) the amount of sulphate formed (where the iron salt originally used was chloride or thiocyanate). The extent of the reduction of the iron was estimated by titration with titanium trichloride, and the sulphate by precipitation with barium chloride, after removal of the iron.

Table II contains a summary of the results obtained from experiments conducted at the ordinary temperature, the quantities being stated in grams per litre of the reaction mixture.

TABLE II.

| Iron salt. | Ferric iron originally present. | Iron reduced during the experiment. | $H_2SO_4$ stated as $BaSO_4$. |  | Carbon dioxide. |  |
|---|---|---|---|---|---|---|
|  |  |  | Found. | Calc. | Found. | Calc. |
| Chloride ......... | 14·26 | 2·42 | 1·28 | 1·26 | 0·249 | 0·238 |
| Sulphate .. ...... | 37·20 | 7·35 | — | — | 0·705 | 0·722 |
| Sulphate ......... | 24·40 | 4·20 | — | — | 0·407 | 0·413 |
| Thiocyanate ...... | 9·60 | 4·69 | 2·54 | 2·44 | — | — |
| Thiocyanate ...... | 9·60 | 4·83 | 2·58 | 2·51 | — | — |

In the first three cases the reaction mixture contained initially 100 grams of potassium thiocyanate per litre. Further, in the first case, so much hydrochloric acid was added that the mixture was one-twentieth normal with respect to this acid. No acid was added in the case of the sulphate experiments, in the second of which air, free from carbon dioxide, was employed instead of nitrogen. The solutions of ferric thiocyanate were prepared by treating freshly precipitated and carefully washed ferric hydroxide with thiocyanic acid, insufficient to dissolve the whole. After some time the excess of ferric hydroxide was removed by filtration, and the filtrate was taken as the reaction mixture. Even by this time considerable reduction had taken place, and since some of the carbon dioxide formed during the reduction might have escaped before the ferric thiocyanate solution was ready, the amount of sulphate only is recorded for the last two experiments in the foregoing table.

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* Special experiments in which a known weight of sodium carbonate was added to an excess of dilute sulphuric acid showed that by the aspiration method carbon dioxide could be extracted almost quantitatively, the deficiency being not more than about 1 per cent.

If it is assumed that corresponding with the reduction of the iron there is an oxidation of the thiocyanate, such that carbon is converted into carbon dioxide, and sulphur into sulphate, whilst nitrogen yields ammonia, it follows that for every eight gram-atoms of iron reduced, there should be formed 1 gram-molecule of carbon dioxide, 1 gram-molecule of sulphuric acid, and 1 gram-molecule of ammonia; that is, for every 4·48 grams of iron reduced there should be formed, on the foregoing assumption, 0·44 gram of carbon dioxide, 0·98 gram of sulphuric acid (=2·33 grams barium sulphate), and 0·17 gram of ammonia. The figures for carbon dioxide and barium sulphate, calculated on this basis from the amount of iron reduced, are shown in the above table alongside the experimentally determined quantities of these substances; it will be seen that there is a very fair agreement between the observed and calculated figures. The ammonia produced in the reaction mixture was determined in one or two cases by adding excess of alkali and distilling into standard acid, but the amount so found was never more than about two-thirds of that calculated on the foregoing basis. It was thought that possibly the estimation of this compound by distillation from an alkaline liquid containing large quantities of potassium thiocyanate might be inaccurate, but special experiments carried out with the object of testing this point showed that ammonia could be recovered quantitatively from such a solution. It is therefore evident that only part of the nitrogen from the oxidised thiocyanate is converted into ammonia, and no definite information has been obtained as to the nature of the other product or products.

In addition to the sulphate and carbon dioxide, which are almost exclusively the products of oxidation at the ordinary temperature, mention should be made of other substances which were detected in very small quantity. These were: (1) hydrocyanic acid, (2) a yellow precipitate, which separated from the reaction mixture, and consisted probably of perthiocyanic acid or ψ-thiocyanogen (compare Chattaway and Stevens, T., 1897, **71**, 607; Stokes and Cain, *J. Amer. Chem. Soc.*, 1907, **29**, 443). The amount of hydrocyanic acid produced was extremely small, as was indicated by weighing the precipitate obtained in the flask containing silver nitrate; this precipitate was shown to contain no thiocyanate. In one experiment in which the amount of iron reduced was 4·2 grams per litre of the reaction mixture, the corresponding silver cyanide precipitate weighed only 0·021 gram.

Experiments similar to the above were carried out at higher temperatures, namely, at 39° and 60°. At the lower temperature air freed from carbon dioxide was aspirated through the apparatus; at the higher temperature, nitrogen freed from carbon dioxide was employed. The quantitative examination of the reaction mixture in all these cases was confined to a determination of (*a*) the amount of iron reduced, and (*b*) the amount of carbon dioxide formed. The results of these experiments are summarised in the following table, in which, as before, the figures indicate grams per litre of the reaction mixture.

TABLE III.

| | | | | Carbon dioxide. | |
|---|---|---|---|---|---|
| Temp. | Iron salt. | Ferric iron originally present. | Iron reduced during the experiment. | Found. | Calc. |
| 39° | Sulphate | 12·70 | 6·34 | 0·622 | 0·622 |
| 39 | Chloride | 10·80 | 3·37 | 0·324 | 0·331 |
| 60 | Sulphate | 16·27 | 12·82 | 1·280 | 1·260 |
| 60 | Sulphate | 42·70 | 16·77 | 1·615 | 1·645 |

In a similar experiment, carried out at 60° with chloride as the iron salt (10·80 grams of iron per litre of the reaction mixture), there was complete reduction in three days, but the amount of carbon dioxide found was 1·16 grams, as compared with 1·06 grams, calculated on the basis described above. In this case, however, there was a large deposit of yellow solid in the reaction flask, and a considerable black precipitate consisting of sulphide and cyanide in the silver nitrate flask, whilst sulphide was detected also in the contents of the first baryta flask. Probably this may be connected with the production of carbonyl sulphide, and its hydrolysis in the absorption flasks; an odour suggestive of this compound was detected on opening the reaction flask. In the sulphate experiments, on the other hand, which are recorded in Table III, the slight precipitate obtained in the silver nitrate flask had merely a grey tinge, and the contents of the first baryta flask were quite free from sulphide. Qualitative experiments at 80° indicated that in the case of both sulphate and chloride, the quantity of hydrocyanic acid produced is much larger than at 60°; further, the mixture of ferric chloride and thiocyanate gave a large, yellow deposit in a comparatively short time. At 100° the mixture of ferric salt and thiocyanate evolves hydrogen sulphide as well as hydrocyanic acid, although this is more marked with the chloride than with the sulphate.

It is worth noting that experiments carried out with ethereal solutions of ferric thiocyanate at the ordinary temperature showed no measurable reduction in two days, although in an aqueous solution, under the same conditions of temperature and concentration, about one-third of the ferric iron would have been reduced in this time.

### *Velocity of the Reaction between Ferric Salts and Thiocyanates.*

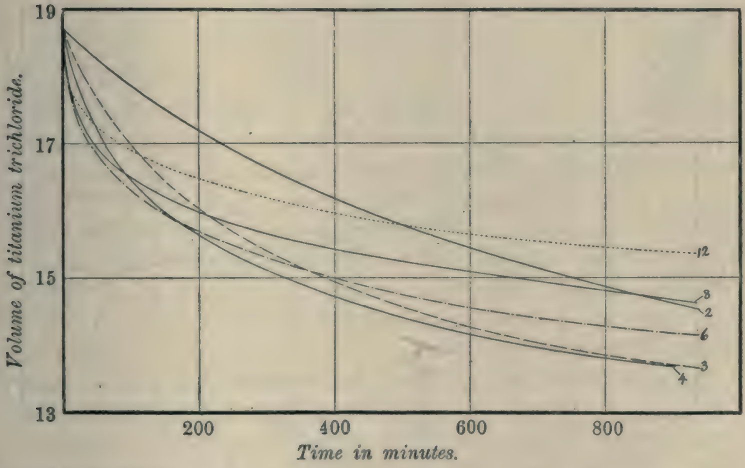
When the thiocyanate is present in a proportion smaller than corresponds with the composition of ferric thiocyanate, $Fe(CNS)_3$, the velocity of reduction, at least in its initial stages, is very much lower than when the thiocyanate is in excess. The variation in the velocity with concentration is clearly shown by a series of experiments, carried out at 25°. In these, a constant quantity of ferric sulphate solution was mixed with different quantities of a strong solution of potassium thiocyanate, the mixture being made up to the same volume in each case. Hence the initial concentration of the iron was the same (8·67 grams of iron per litre) in each experiment of the series, whilst the concentration of the thiocyanate varied. The volume of a standard titanium trichloride solution required initially for 5 c.c. of each mixture was 18·70 c.c., and the following tables show the volumes of titanium trichloride required at intervals for 5 c.c. of the different mixtures.

TABLE IV.

| | Time in minutes. | Vol. $TiCl_3$. | | Time in minutes. | Vol. $TiCl_3$. |
|---|---|---|---|---|---|
| 1Fe : 2KCNS. | 0 | 18·70 | 1Fe : 6KCNS. | 0 | 18·70 |
| | 67 | 18·10 | | 23 | 17·30 |
| | 157 | 17·45 | | 55 | 16·75 |
| | 297 | 16·68 | | 95 | 16·35 |
| | 496 | 15·82 | | 281 | 15·38 |
| | 680 | 15·23 | | 573 | 14·61 |
| | 880 | 14·67 | | 865 | 14·23 |
| | [120 hours | 11·50] | | [120 hours | 13·35] |
| 1Fe : 3KCNS. | 0 | 18·70 | 1Fe : 8KCNS. | 0 | 18·70 |
| | 31 | 18·00 | | 18 | 17·50 |
| | 64 | 17·40 | | 50 | 16·95 |
| | 213 | 15·90 | | 138 | 16·30 |
| | 390 | 15·00 | | 372 | 15·50 |
| | 590 | 14·32 | | 660 | 15·00 |
| | 877 | 13·74 | | 857 | 14·75 |
| | [120 hours | 12·00] | | [120 hours | 14·05] |
| 1Fe : 4KCNS. | 0 | 18·70 | 1Fe : 12KCNS. | 0 | 18·70 |
| | 30 | 17·65 | | 12 | 17·75 |
| | 61 | 16·95 | | 46 | 17·30 |
| | 150 | 16·00 | | 82 | 17·00 |
| | 290 | 15·18 | | 189 | 16·50 |
| | 586 | 14·20 | | 559 | 15·68 |
| | 873 | 13·73 | | 849 | 15·43 |
| | [120 hours | 12·40] | | [120 hours | 14·90] |

The results recorded in the foregoing table are represented graphically by the curves in Fig. 1, which are numbered according to the initial molecular proportion of potassium thiocyanate to one atom of iron. It will be seen that, although the very first portions of the curves which correspond with the ratios 1 : 6, 1 : 8, and 1 : 12 are practically indistinguishable, yet clearly the initial rate of reduction is much greater when the proportion of thiocyanate is high than when it is low; as time proceeds, however, the velocities in the former case fall off more rapidly than in the latter case. A striking illustration of this is furnished by the curves for the proportions 1Fe : 2KCNS, and 1Fe : 12KCNS. The latter curve in its early course is very steep, but the slope soon falls off, and the curve is cut by the curve 2, the slope of which, although much less steep at the beginning, remains more uniform. A study of the figure will show that the other curves are of a character intermediate between these two extreme cases. Further, titrations of the mixtures made some days later (see figures in brackets in the foregoing table) showed clearly that the reaction had proceeded farthest in the mixture containing the smallest proportion of thiocyanate, and had made least progress in the case where the initial concentration of thiocyanate was greatest. It should be mentioned that similar experiments to those recorded in Table IV were made at 40°, and the character of the curves obtained exhibits a close resemblance to those shown in Fig. 1.

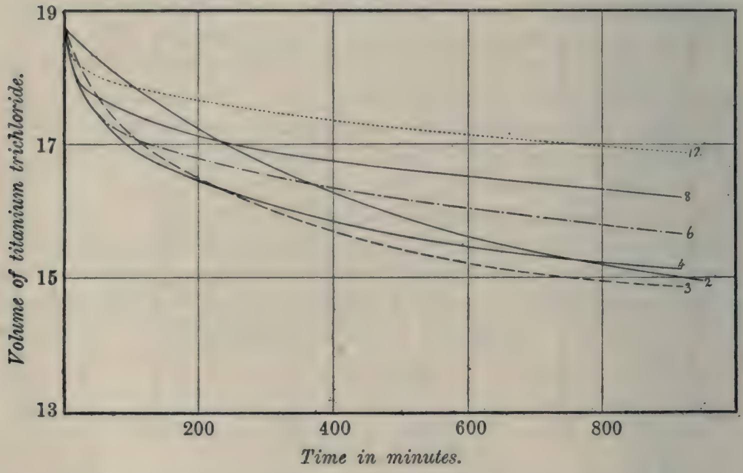
Fig. 1.



It is obvious that the influence of mass on the velocity of reduction of ferric salts by thiocyanates is not capable of any simple mathematical formulation, but the following experiments appear to indicate that the acid produced in the reduction of the ferric salt is mainly responsible for the peculiar relationships expressed in Table IV and Fig. 1.

The initial addition of acid to mixtures of ferric sulphate and potassium thiocyanate produces an effect which depends on the relative proportions of the iron and the thiocyanate. When the thiocyanate is in very large excess, the presence of acid markedly retards the reaction, whilst with the ratio 1Fe : 1·5KCNS the velocity, at least for the first third of the change, is the same whether acid has been added or not.

FIG. 2.



The evidence bearing on the influence of acids is incorporated in Table V and Fig. 2. These experiments were in all respects parallel to those recorded in Table IV, except that all the solutions were now initially made 0·25*N* with respect to sulphuric acid. The concentrations of ferric sulphate and potassium thiocyanate were exactly the same as for the six mixtures already investigated, and the temperature was 25°.

TABLE V.

|  | Time in minutes. | Vol. $TiCl_3$. |  | Time in minutes. | Vol. $TiCl_3$. |
|---|---|---|---|---|---|
| 1Fe : 2KCNS. | 0 | 18·70 | 1Fe : 6KCNS. | 0 | 18·70 |
|  | 35 | 18·40 |  | 23 | 17·84 |
|  | 70 | 18·10 |  | 58 | 17·42 |
|  | 179 | 17·35 |  | 105 | 17·10 |
|  | 345 | 16·48 |  | 241 | 16·66 |
|  | 585 | 15·65 |  | 573 | 16·05 |
|  | 830 | 15·15 |  | 818 | 15·76 |
|  | [28 hours | 14·07] |  | [28 hours | 15·35] |

TABLE V. (*continued*).

| | Time in minutes. | Vol. $TiCl_3$. | | Time in minutes. | Vol. $TiCl_3$. |
|---|---|---|---|---|---|
| 1Fe : 3KCNS. | 0 | 18·70 | 1Fe : 8KCNS. | 0 | 18·70 |
| | 31 | 18·06 | | 19 | 17·97 |
| | 66 | 17·50 | | 54 | 17·70 |
| | 113 | 17·01 | | 101 | 17·45 |
| | 251 | 16·27 | | 330 | 16·85 |
| | 586 | 15·27 | | 566 | 16·55 |
| | 826 | 14·95 | | 818 | 16·30 |
| | [28 hours | 14·25] | | [28 hours | 15·90] |
| 1Fe : 4KCNS. | 0 | 18·70 | 1Fe : 12KCNS. | 0 | 18·70 |
| | 27 | 17·76 | | 15 | 18·24 |
| | 62 | 17·30 | | 50 | 18·03 |
| | 108 | 16·85 | | 97 | 17·87 |
| | 247 | 16·27 | | 230 | 17·60 |
| | 442 | 15·80 | | 425 | 17·30 |
| | 822 | 15·20 | | 810 | 16·98 |
| | [28 hours | 14·58] | | [28 hours | 16·62] |

The results recorded in the foregoing table are represented graphically in Fig. 2, which is on the same scale as Fig. 1. A comparison will show that whereas curve 2 is only slightly higher in Fig. 2 than in Fig. 1, curve 12 is displaced upwards to a very notable extent, whilst the displacement of the other curves is intermediate. The different influence of acid on the velocities for the 1 : 2 and 1 : 12 mixtures is well shown by the different positions of the points of intersection of the corresponding curves. It is interesting to note, also, that the extent of reduction in the 1 : 2 mixtures was, after twenty-eight hours, greater than in any of the other mixtures (see foregoing table).

It appears from these results that the peculiar relationship of the curves shown in Fig. 1 is probably connected with the presence of acid; this, as shown by the equation suggested on p. 796, is produced in the course of the reduction, and its amount obviously increases with time. Now experiments with solutions which contained initially the same amounts of ferric sulphate and potassium thiocyanate, but different quantities of sulphuric acid, have shown that the rate of reduction diminishes as the concentration of acid increases. The ratio Fe : KCNS in these experiments was 1 : 4, and the temperature was 25°. The figures in the following table represent the volumes of titanium trichloride required for a given volume of four reaction mixtures, the first of which contained no added acid, whilst the others were initially made 0·25*N*, 0·50*N*, and 1·00*N* with respect to sulphuric acid.

TABLE VI.

| Time in minutes. | No acid. | 0·25$N$-$H_2SO_4$. | 0·5$N$-$H_2SO_4$. | 1·0$N$-$H_2SO_4$. |
|---|---|---|---|---|
| 0 | 63·5 | 63·5 | 63·5 | 63·5 |
| 50 | 61·5 | 62·3 | 62·8 | 63·1 |
| 100 | 60·6 | 61·6 | 62·3 | 62·8 |
| 200 | 59·6 | 60·8 | 61·7 | 62·3 |

Another factor that bears on the peculiar character of the curves in Fig. 1 is the progressive diminution in the ratio of ferric iron to thiocyanate, which, on the basis of the equation on p. 796, is involved in the reaction. This circumstance, as well as the gradually increasing quantity of acid present, would tend to bring about a retardation of the reduction.

Experiments were also made on the influence of acids for solutions in which the initial ratio of ferric iron to thiocyanate was greater than 1 : 2. Ammonium thiocyanate was employed in these experiments, the initial ratio Fe : $NH_4CNS$ being 1 : 0·9 in each case. The effects of different quantities of sulphuric acid are shown in Table VII, the figures in which, like those in Table VI, represent the volumes of titanium trichloride solution required for a given volume of the reaction mixture. The temperature was 60°.

TABLE VII.

| Time in minutes. | No acid. | 0·1*N*-$H_2SO_4$. | 0·2*N*-$H_2SO_4$. | 0·4*N*-$H_2SO_4$. |
|---|---|---|---|---|
| 0 | 49·0 | 49·0 | 49·0 | 49·0 |
| 20 | 42·7 | 42·1 | 40·7 | 39·6 |
| 50 | 37·6 | 36·6 | 35·0 | 33·5 |
| 100 | 32·7 | 31·6 | 30·0 | 28·6 |

It will be seen that the greater the initial concentration of acid the greater is the velocity of reduction. Similar experiments, carried out at 40° with two solutions of ferric sulphate and potassium thiocyanate (ratio 1Fe : 1KCNS), one of which contained no added acid, and the other was initially 0·25*N* with respect to sulphuric acid, confirmed the view that for this ratio of ferric iron to thiocyanate, acid definitely accelerates the reduction.

An attempt was made to secure evidence bearing on the order of the reaction between ferric salts and thiocyanates by experiments in which the thiocyanate was in very large excess, whilst the concentration of the iron salt varied. In these experiments, three of which, carried out at 40°, are recorded below in Table VIII, the

TABLE VIII.

| Fractional reduction of the iron. | Times in minutes. | | |
|---|---|---|---|
| | *a.* | *b.* | *c.* |
| 0·05 | 1·5 | 1·7 | 2·0 |
| 0·10 | 4·0 | 4·0 | 4·0 |
| 0·15 | 7·7 | 7·8 | 7·7 |
| 0·20 | 13·5 | 14·6 | 14·0 |
| 0·25 | 23·3 | 25·6 | 26·7 |
| 0·30 | 42·6 | 47·5 | 49·0 |
| 0·35 | 75·0 | 82·5 | 89·0 |
| 0·40 | 122·0 | 137·5 | 158·0 |

initial concentration of ammonium thiocyanate was in each case 75 grams per litre; in (*a*) the ratio of iron to thiocyanate, Fe : $NH_4CNS$, was 1 : 18, in (*b*), 1 : 13·5, and in (*c*), 1 : 9. The curves representing the rate of reduction were deduced as usual, and from these the times (in minutes) necessary for a given fractional reduction of the iron were read off. These times are recorded in Table VIII.

From the figures in the table it is apparent that, where the thiocyanate is in large excess and for the first quarter of the reaction, the time necessary for the reduction of a given fraction of the iron is almost independent of the initial concentration of the iron. The conclusion may be drawn therefore that in its early stages the reaction is unimolecular with respect to the iron. After the first portion of the change is over, the foregoing simple relationship holds no longer, the time necessary for the completion of a given fractional reduction being then least for (*a*), and greatest for (*c*). In view of the effect of acids on the rate of reduction, it is not surprising that the course of the reaction cannot be formulated on the usual lines. Further experiments are being made with the object of gaining further information as to the mechanism of the change.

The influence of temperature on the velocity of interaction of ferric salts and thiocyanates is very marked. It is not possible to state the value of the temperature-coefficient, but an idea of the relative velocities at different temperatures may be gained from the following observations. Experiments made with a given mixture of ferric sulphate and potassium thiocyanate (ratio (1Fe : 2KCNS) at two temperatures, 25° and 40°, showed that the times necessary for the reduction of one-fifth of the iron were respectively 760 and 94 minutes.

It was thought that the velocity of the reaction between ferric salts and thiocyanates might be affected by light. Experiments were therefore made in which equal portions of a given mixture of ferric sulphate and potassium thiocyanate were placed in narrow test-tubes, and either kept in the dark or exposed to diffuse daylight. It was found after four weeks that the extent of reduction in the exposed tubes was exactly the same as in those which had been kept in the dark. It was observed, however, that the slight yellow deposit obtained in all the solutions formed preferentially, in the case of those exposed to light, on the wall of the tube next the light.

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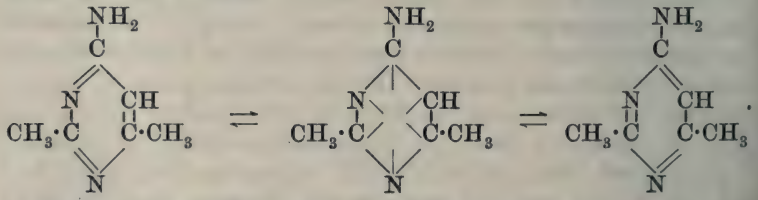
# LXXXIII.—*Non-aromatic Diazonium Salts. Part I. Antipyrinediazonium Salts and their Azo-derivatives.*

By GILBERT T. MORGAN and JOSEPH REILLY, B.A., B.Sc., A.R.C.Sc.I.

THE greatest development in the chemistry of diazo-compounds has taken place in connexion with aromatic amines, owing mainly to two facts: the important technical employment of benzenoid and naphthalenoid diazo-derivatives in the manufacture of azo-dyes, and the manifold applications of the diazo-reaction to synthetic operations in the aromatic series.

It is, however, known that certain non-aromatic amines possess in varying degrees the property of diazotisability, and the object of the present investigation is to ascertain within what limits this reaction is manifested by bases which do not contain amino-groups attached to aromatic nuclei. The property of diazotisability appears to be connected with the presence in the basic molecule of an unsaturated group, for hitherto it has not been found possible to diazotise the salt of any primary base having its amino-group attached either to a fully saturated radicle or to a completely hydrogenised ring. These two cases may be exemplified respectively by the aliphatic primary amines and by bornylamine and *ac*-tetrahydro-$\beta$-naphthylamine. On the other hand, there are many bases with amino-groups attached to unsaturated complexes which are not diazotisable.

For example, the authors have not succeeded in diazotising 6-amino-2:4-dimethylpyrimidine (cyanmethine), a base possessing a six-membered cyclic ring closely akin to that of the benzene nucleus, with the same possibility of ethenoid and centric arrangements of the valencies:



In spite of the close analogy to aniline and its homologues, this base behaves as an aliphatic amine, and yields the corresponding 6-hydroxy-2:4-dimethylpyrimidine on treatment with nitrous acid.*

The orientation of the amino-group in the foregoing base with regard to cyclic nitrogen is, in all probability, not without importance, for Mills and Watson have shown that 3-aminoquinoline is readily diazotisable, differing in that respect from 2- and 4-aminoquinolines, which have not yielded diazonium salts (T., 1910, **97**, 741).

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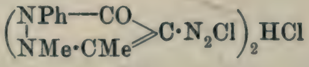
* It has recently been noticed (this vol., p. 72) that 2-amino-1:4-naphthaquinoneimide is not diazotisable, although the basic group is attached to an unsaturated complex derived from dihydronaphthalene.

The researches of Knorr and his collaborators have demonstrated that certain bases of the pyrazole series are diazotisable, giving rise to very stable diazo-derivatives, which, however, have hitherto only been obtained in solution. These diazo-compounds, like the aromatic diazonium salts, couple with alkaline β-naphthol, and furnish diazoamines with aniline, but with the exception of the preparation of triazoantipyrine by Forster and Müller (T., 1909, **95**, 2072), they have not been employed successfully in syntheses involving the replacement of the diazo-group by other radicles.

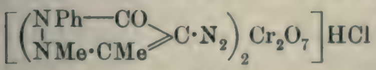
As a preliminary step in the closer study of the diazo-derivatives of the pyrazole series, the authors have isolated 1-*phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium chloride*, produced by diazotising 4-amino-1-phenyl-2 : 3-dimethylpyrazolone (4-aminoantipyrine). The hydrochloride of this base, when treated with ethyl nitrite in alcoholic solution, yields, on concentration, a syrupy residue, but when diazotisation is effected in the presence of excess of hydrochloric acid, a crystalline, hygroscopic salt is obtained having the following constitution:



$$\left(\begin{array}{l}\text{NPh—CO}\\ \text{NMe·CMe}\end{array}\!\!>\text{C·N}_2\text{Cl}\right)_2\text{HCl}$$

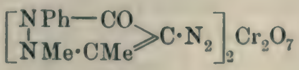
(I.)

The additional molecule of hydrogen chloride is probably attracted to the complex by the basic nitrogen atoms of the pyrazolone rings, but it should be mentioned that acid diazonium salts have been observed in the aromatic series, although in such cases their stability has been less than that of the normal salts (Hirsch, *Ber.*, 1897, **30**, 1148; Hantzsch, *ibid.*, 1153). From the foregoing acid chloride the corresponding *dichromate hydrochloride* was obtained, which, when dried under diminished pressure over potassium hydroxide, slowly lost its volatile acid, and became converted into the normal *dichromate*:



$$\left[\left(\begin{array}{l}\text{NPh—CO}\\ \text{NMe·CMe}\end{array}\!\!>\text{C·N}_2\right)_2\text{Cr}_2\text{O}_7\right]\text{HCl}$$

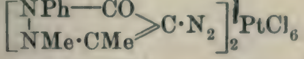
(II.)



$$\left[\begin{array}{l}\text{NPh—CO}\\ \text{NMe·CMe}\end{array}\!\!>\text{C·N}_2\right]_2\text{Cr}_2\text{O}_7$$

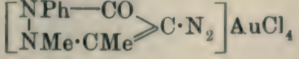
(III.)

The *platinichloride* and *aurichloride* containing the normal amounts of acidic constituents have also been obtained.



$$\left[\begin{array}{l}\text{NPh—CO}\\ \text{NMe·CMe}\end{array}\!\!>\text{C·N}_2\right]_2\text{PtCl}_6$$

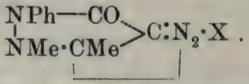
(IV.)



$$\left[\begin{array}{l}\text{NPh—CO}\\ \text{NMe·CMe}\end{array}\!\!>\text{C·N}_2\right]\text{AuCl}_4$$

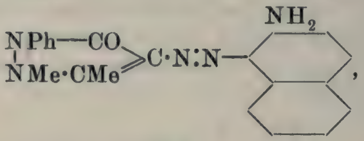
(V.)

The existence of these normally constituted diazonium salts containing the pyrazolone ring is of some interest in connexion with current theories of the structure of diazo-compounds, inasmuch as it justifies the contention that co-ordination between the diazonium complex and the unsaturated ring may involve a contiguous carbon atom as well as one in the para-position (T., 1907, **91**, 1315; 1908, **93**, 617). The para-hemiquinonoid formula advocated by Cain is inapplicable to these pyrazolonediazonium salts (compare Forster and Müller, *loc. cit.*). Representing this co-ordination as being due to a rearrangement in the principal valencies, then the general formula for these diazonium salts would be:



$$\begin{matrix}\text{NPh—CO}\\ |\\ \text{NMe·CMe}\end{matrix}>C{:}N_2{\cdot}X\ .$$

1-Phenyl-2 : 3-dimethylpyrazolone-4-diazonium chloride couples readily with the more reactive aromatic bases yielding azo-derivatives. With *m*-phenylenediamine, it furnishes an azo-colour of the chrysoidine group, and with β-naphthylamine it gives rise to 1-*phenyl*-2 : 3-*dimethylpyrazolone*-4-*azo*-β-*naphthylamine*:

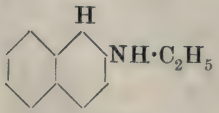


(VI.)

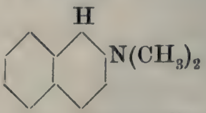
an aminoazo-derivative distinguished from the arylazo-β-naphthylamines by its power of forming intense bluish-purple salts with mineral or organic acids, which are so stable in aqueous solution that the azo-base can be used as an indicator in acidimetry and alkalimetry. This property, like that of forming the foregoing acid diazonium chloride, is to be correlated with the basic nature of the pyrazolone ring.

An interesting parallelism was noticed in the coupling of the antipyrinediazonium salts with β-naphthylamine and its derivatives on the one hand, and the β-diketones and β-keto-esters on the other. In both cases the condensation takes place only when two mobile hydrogen atoms are present.

An azo-derivative is readily produced from ethyl-β-naphthylamine (VII), but no reaction takes place with dimethyl-β-naphthylamine (VIII), which has only the one reactive hydrogen atom:

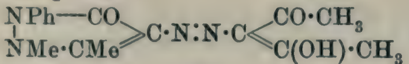


(VII.) Coupling.



(VIII.) Non-coupling.

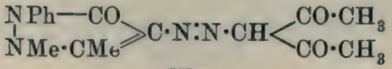
Acetylacetone and the antipyrinediazonium salts readily couple, yielding an azo-compound:



$$\begin{array}{l}NPh{-}CO\\ NMe\cdot CMe\end{array}\!\!>C\cdot N{:}N\cdot C\!<\!\begin{array}{l}CO\cdot CH_3\\ C(OH)\cdot CH_3\end{array}$$

(IX.)

or

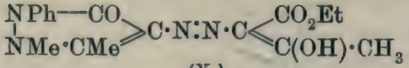


$$\begin{array}{l}NPh{-}CO\\ NMe\cdot CMe\end{array}\!\!>C\cdot N{:}N\cdot CH\!<\!\begin{array}{l}CO\cdot CH_3\\ CO\cdot CH_3\end{array}$$

(IX*a*.)

The azo-constitution for this substance, 1-*phenyl*-2:3-*dimethylpyrazolone*-4-*azoacetylacetone*, is justified by the fact that it yields, even in aqueous solution, a sparingly soluble alkali derivative, which develops the enolic red coloration with ferric chloride and furnishes an olive-green copper derivative. These reactions render very improbable a hydrazone configuration, and support the enolic formula (IX) for the sodium derivative; they do not, however, serve to exclude the ketonic constitution (IX*a*) for the free azo-compound.

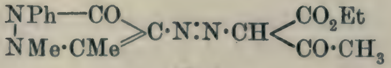
*Ethyl* 1-*phenyl*-2:3-*dimethylpyrazolone*-4-*azoacetoacetate* (X or X*a*) closely resembles the foregoing azo-acetylacetone, and is obtained under precisely similar conditions:



$$\begin{array}{l}NPh{-}CO\\ NMe\cdot CMe\end{array}\!\!>C\cdot N{:}N\cdot C\!<\!\begin{array}{l}CO_2Et\\ C(OH)\cdot CH_3\end{array}$$

(X.)

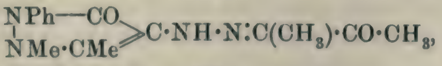
or



$$\begin{array}{l}NPh{-}CO\\ NMe\cdot CMe\end{array}\!\!>C\cdot N{:}N\cdot CH\!<\!\begin{array}{l}CO_2Et\\ CO\cdot CH_3\end{array}$$

(X*a*.)

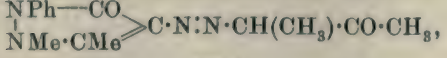
With methyl acetylethyl ketone, $CH_3\cdot CO\cdot \overset{*}{C}H(CH_3)\cdot CO\cdot CH_3$, which, like dimethyl-β-naphthylamine, contains only one labile hydrogen (*), the reaction takes a different course. Coupling occurs, but it is accompanied by hydrolysis, involving the elimination of an acetyl group, so that the parent ketone is ethyl methyl ketone. The pale yellow product differs from the antipyrylazoacetylacetone in not giving an alkali derivative with aqueous sodium hydroxide. This difference may be explained by regarding the compound as an antipyrylhydrazone of dimethyl diketone:



$$\begin{array}{l}NPh{-}CO\\ NMe\cdot CMe\end{array}\!\!>C\cdot NH\cdot N{:}C(CH_3)\cdot CO\cdot CH_3,$$

(XI.)

or as an antipyrylazo-derivative of ethyl methyl ketone:



$$\begin{array}{l}NPh{-}CO\\ NMe\cdot CMe\end{array}\!\!>C\cdot N{:}N\cdot CH(CH_3)\cdot CO\cdot CH_3,$$

XI*a*.)

which is no longer capable of assuming the enolic form, and therefore does not yield metallic derivatives.

The study of these condensation products from antipyrinediazonium salts and the β-diketo-compounds is being continued.

## EXPERIMENTAL.

### 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium Chloride* (Formula I).

4-Aminoantipyrine hydrochloride (m. p. 232°), obtained by successively reducing 4-nitrosoantipyrine, extracting the crude base in the form of its benzylidene derivative, hydrolysing the latter with dilute hydrochloric acid, and removing the benzaldehyde with ether, was purified by repeated crystallisation from alcohol, and used in the following experiments.

(1) The diazo-solution, produced by treating the purified salt with ethyl nitrite in absolute alcohol, left on evaporation a syrupy residue, which after two months had lost its power of coupling with alkaline β-naphthol.

(2) The salt dissolved in alcohol containing hydrochloric acid (3 mols.) was treated with ethyl nitrite in slight excess. The solution was concentrated in a vacuum desiccator over potassium hydroxide until the acid diazonium chloride separated in stellate aggregates of almost colourless, hygroscopic crystals, which retained their coupling power with β-naphthol after three months:

0·1468 gave 0·2596 $CO_2$ and 0·0485 $H_2O$. C = 48·23; H = 3·68.
0·1215 „ 21·6 $N_2$ at 17° and 752 mm.* N = 20·63.
0·1605 „ 0·1272 AgCl. Cl = 19·61.
0·1422 „ 0·1115 AgCl. Cl = 19·39.
$(C_{11}H_{11}ON_4Cl)_2,HCl$ requires C = 49·12; H = 4·28; N = 20·85; Cl = 19·79 per cent.

The chlorine determinations were made on different preparations, one of which had been heated on the water-bath in alcoholic solution in order to remove excess of ethyl nitrite. The diazonium chloride was insoluble in dry ether.

Reduction of this diazonium salt with stannous chloride does not lead to the formation of a readily isolated hydrazine, owing probably to condensation taking place between the newly formed hydrazino-group and the carbonyl radicle present in the pyrazolone ring.

The diazonium chloride and the corresponding nitrate were both very stable in hot aqueous solutions, but the coupling power, which persisted under these conditions, disappeared entirely when the chloride was digested with moist silver oxide, the filtrate from silver chloride giving no azo-colour. When treated successively with sodium hydroxide (3 mols.) and cold dilute acetic acid, the diazonium salt lost completely its coupling power. Potassium cyanide added to an acid solution of the diazonium salt had the same destructive effect; a white, unstable diazo-cyanide was precipitated, which rapidly became yellow, and then black. Potassium thiocyanate produced a white precipitate with the diazonium chloride, which darkened on exposure to air.

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* In this and the following nitrogen estimations the gas was measured over 50 per cent. potassium hydroxide solution.

### 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium Dichromate Hydrochloride* (Formula II).

The salt separated in orange-yellow, acicular crystals on adding aqueous chromium trioxide to a solution of the acid diazonium chloride:

0·1922 gave 0·0428 AgCl and 0·0425 $Cr_2O_3$. Cl = 5·51; Cr = 15·13.

$C_{22}H_{23}O_9N_8ClCr_2$ requires Cl = 5·20; Cr = 15·24 per cent.

When dried for several weeks in a vacuum desiccator over solid potassium hydroxide, hydrogen chloride was slowly eliminated, and although the salt still contained some chlorine (Cl = 1·99 per cent.), its composition now corresponded closely with that of 1-*phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium dichromate* (III):

0·1940 gave 0·0460 $Cr_2O_3$. Cr = 16·22.
0·2868 „ 0·0673 $Cr_2O_3$. Cr = 16·05.
0·1620 „ 24·5 c.c. $N_2$ at 21·5° and 765 mm. N = 17·54.
0·0976 „ 14·6 c.c. $N_2$ „ 21° „ 765 mm. N = 17·38.

$C_{22}H_{22}O_9N_8Cr_2$ requires Cr = 16·10; N = 17·34 per cent.

The dichromate, although stable at the ordinary temperature, exploded on heating or by percussion. When heated to 120° in a strong aqueous solution of sulphuric acid, only about half the diazo-nitrogen was eliminated.

### 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium Platinichloride* (Formula IV).

On mixing aqueous solutions of chloroplatinic acid and the foregoing diazonium chloride, an almost quantitative precipitation occurred of the crystalline, yellow diazonium platinichloride. This salt, after drying in the desiccator, remained constant in weight up to 120°:

0·1648 gave 0·1920 $CO_2$ and 0·0455 $H_2O$. C = 31·77; H = 3·07.
0·2477 „ 29·8 c.c. $N_2$ at 20° and 751 mm. N = 13·75.
0·1492 „ 17·8 c.c. $N_2$ „ 20° „ 746 mm. N = 13·55.
0·2278 „ 0·233 AgCl. Cl = 25·30.
0·1161 „ 0·0271 Pt. Pt = 23·34.

$C_{22}H_{22}O_2N_8Cl_6Pt$ requires C = 31·50; H = 2·63; N = 13·37; Cl = 25·38; Pt = 23·29 per cent.

### 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium Aurichloride* (Formula V).

This salt was obtained as a golden-yellow, crystalline precipitate on mixing aqueous solutions of the diazonium chloride and chloroauric acid:

0·1520 gave 0·1330 $CO_2$ and 0·0323 $H_2O$. C = 23·86; H = 2·36.
0·1893 „ 16·6 c.c. $N_2$ at 17° and 758 mm. N = 10·25.
0·1476 „ 0·1535 AgCl. Cl = 25·72.
0·1890 „ 0·0672 Au. Au = 35·55.
$C_{11}H_{11}ON_4Cl_4Au$ requires C = 23·83; H = 1·99; N = 10·11; Cl = 25·60; Au = 35·59 per cent.

The three foregoing diazonium salts are all very stable compounds, coupling with alkaline β-naphthol after several months to form a red azo-compound. In the case of the aurichloride the red colour soon changes to brown unless the gold is previously removed as sulphide, when the red coloration persists.

### 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*azo*-β-*naphthylamine* (Formula VI).

On adding a solution in dilute hydrochloric acid of the diazonium chloride to alcoholic β-naphthylamine, a deep blue coloration was immediately developed, and the solution rapidly became almost solid, owing to the separation of the sparingly soluble, dark blue hydrochloride of the aminoazo-derivative. From this salt the aminoazo-base was set free by ammonia and crystallised repeatedly from alcohol, in which it was somewhat sparingly soluble. The base separated in orange-red biaxial needles, darkening at 234°, and melting at 235°:

0·0635 gave 10·9 c.c. $N_2$ at 20° and 755 mm. N = 19·73.
$C_{21}H_{19}ON_5$ requires N = 19·61 per cent.

This azo-base was sparingly soluble in the ordinary volatile organic media, more soluble in pyridine, but insoluble in water.

The *hydrochloride* was prepared by dissolving the base in glacial acetic acid, and adding hydrochloric acid; it crystallised in tufts of small, acicular, bluish-black crystals, with blonzy reflex, and decomposed at 185°:

0·1365 gave 20·5 c.c. $N_2$ at 17° and 765 mm. N = 17·72.
0·2630 „ 0·0970 AgCl and 0·2381 base. Cl = 9·12; Base = 90·53.
$C_{21}H_{19}ON_5,HCl$ requires N = 17·79; Cl = 9·01; Base = 90·73 per cent.

This salt was sparingly soluble in water and the ordinary organic media, but dissolved more readily in pyridine.

Comparative experiments were made with ethyl-β-naphthylamine and dimethyl-β-naphthylamine. The former of these bases coupled with 1-phenyl-2 : 3-dimethylpyrazolonediazonium chloride in alcoholic solution, giving rise to an orange azo-derivative, which separated from alcoholic hydrochloric acid in the form of its dark, bronzy-blue hydrochloride.

Dimethyl-β-naphthylamine did not couple with the diazonium salt under the foregoing experimental conditions, and the greater portion of the base was recovered unchanged.

β-Naphthylamine-6-sulphonic acid (Brönner acid), when dissolved in aqueous sodium carbonate and reprecipitated by acetic acid, coupled readily with the diazonium hydrochloride, yielding a dark blue azo-derivative (hydrochloride), which is decomposed by aqueous sodium acetate, giving rise to the reddish-orange azo-sulphonic acid.

The three foregoing azo-derivatives dissolved in concentrated sulphuric acid to deep red solutions, which assumed an intensely purple shade on dilution with water.

1-Phenyl-2 : 3-dimethylpyrazoloneazo-β-naphthol, unlike the purely aromatic azo-β-naphthols, assumes a dark reddish-purple tint on treatment with concentrated aqueous acids, its original colour, orange-red, being restored by alkalis.

### *Condensation Products with the β-Diketones.*

### 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*azoacetylacetone* (Formula IX or IX*a*).

4-Aminoantipyrine hydrochloride (1 mol.) was diazotised in cold dilute hydrochloric acid, the excess of nitrous acid removed by carbamide, and the solution added to acetylacetone (1 mol.) dissolved in alcohol. The addition of sodium acetate produced a yellow precipitate, which, when crystallised repeatedly from alcohol, separated in radiating masses of reddish-orange scales and biaxial, prismatic needles, melting at 181—182°:

0·1318 gave 0·2955 $CO_2$ and 0·0656 $H_2O$. C = 61·15; H = 5·53.

0·1700 „ 26·6 c.c. $N_2$ at 20° and 752 mm. N = 17·93.

$C_{16}H_{18}O_3N_4$ requires C = 61·15; H = 5·73; N = 17·83 per cent.

This azo-compound was practically insoluble in water, sparingly soluble in ether, but dissolving more freely in other organic media, especially in chloroform.

Benzoylacetone, when coupled with the diazonium salt, gave a similar yellow azo-derivative.

1-Phenyl-2 : 3-dimethylpyrazolone-4-azoacetylacetone yielded a sparingly soluble, dark orange sodium derivative when treated with an excess (2 mols.) of concentrated aqueous sodium hydroxide. With ferric chloride the dilute aqueous solution of the sodium derivative developed an intense red coloration, and with copper sulphate an olive-green copper derivative was precipitated.

### *Ethyl* 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*azoacetoacetate* (Formula X or X*a*).

The antipyrinediazonium solution (1 mol.), prepared as in the preceding experiment, was added to an alcoholic solution of ethyl acetoacetate (1 mol.), followed by excess of sodium acetate. The product, a bulky, yellow precipitate, was crystallised repeatedly from alcohol, when it separated in fibrous masses of yellow, prismatic needles, melting at 174—175°:

0·1226 gave 0·2680 $CO_2$ and 0·0663 $H_2O$. C=59·62; H=6·01.
0·1826 „ 25·5 c.c. $N_2$ at 15·5° and 748 mm. N=16·21.
$C_{17}H_{20}O_4N_4$ requires C=59·30; H=5·81; N=16·28 per cent.

The azo-compound was sparingly soluble in water, ether, or ethyl acetate; it dissolved more readily in other organic media, and especially in chloroform.

### *Condensation Product of* 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium Chloride and Methyl Acetylmethyl Ketone* (Formula XI or XI*a*).

The antipyrinediazonium chloride solution, freed from excess of nitrous acid, was added to alcoholic methyl acetylmethyl ketone (1 mol.). On adding aqueous sodium acetate, a pale yellow precipitate was slowly formed, which, when crystallised repeatedly from alcohol, separated in lustrous, pale yellow, six-sided biaxial plates, melting at 199—200°:

0·2006 gave 0·4635 $CO_2$ and 0·1175 $H_2O$. C=63·02; H=6·51.
0·1706 „ 28·9 c.c. $N_2$ at 18° and 756 mm. N=19·67.
$C_{15}H_{18}O_2N_4$ requires C=62·94; H=6·29; N=19·58 per cent.

The compound is less soluble than the preceding substances in the ordinary organic media, but it dissolved freely in chloroform or pyridine. With aqueous sodium hydroxide it gave no sodium derivative.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,
DUBLIN.

# LXXXIV.—*The Constitution of the Anhydro-bases derived from Tetrahydroberberine Alkyl Hydroxides.*

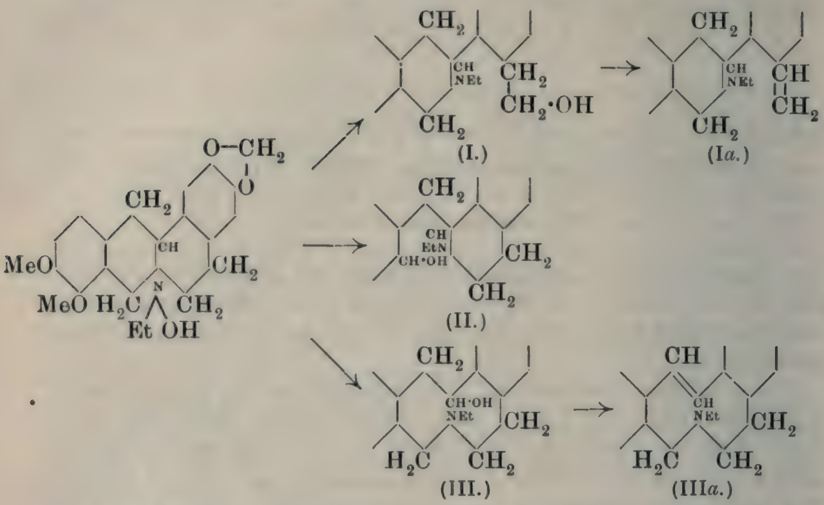
By **Frank Lee Pyman.**

The degradation of tetrahydroberberine by Hofmann's method, that is, the removal of the elements of water from tetrahydroberberine alkyl hydroxides has been the subject of several previous investigations.

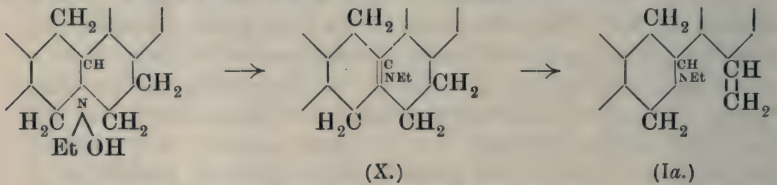
The point was first studied by E. Schmidt and his pupils, Court, Schreiber, Gaze, and Link (*Arch. Pharm.*, 1890, **228**, 596, 604; 1892, **230**, 287, 291; and *Dissertations*), the effect of heating the metho- and etho-hydroxides of tetrahydroberberine being examined. The resulting compounds, however, did not agree in their properties with those to be expected from true anhydro-bases, as E. Schmidt himself (*Arch. Pharm.*, 1892, **230**, 289) points out, since tetrahydroberberine alkyl iodides were regenerated from them by the action of alkyl iodides, whereas unsaturated alkyl iodide additive products should have been obtained.

Voss and Gadamer (*Arch. Pharm.*, 1910, **248**, 43), who next studied this subject, offered further evidence that the products obtained by the previous investigators were not the true anhydro-bases. These authors were the first to isolate a true anhydro-base derived from tetrahydroberberine. They dried tetrahydroberberine ethocarbonate in a vacuum on the water-bath to constant weight, and isolated from the product the ethyl anhydro-base, which melted at 132·5°. They also obtained the same base by evaporating *l*-canadine (*l*-tetrahydroberberine) ethohydroxide to dryness in a vacuum and working up the product so obtained; in this case, however, the presence of another product was observed, for the crude ether-soluble product (which would contain only tertiary bases, such as anhydro- and possibly carbinol bases) proved to be optically active, but the identity of this by-product was left to be cleared up later. The fact that the ethyl anhydro-base, melting at 132·5° was obtained from *l*-canadine as well as from tetrahydroberberine enabled Voss and Gadamer to deduce its constitution as follows.

Tetrahydroberberine ethohydroxide is capable of yielding three hypothetical carbinol bases, I, II, III, of which two, I and III, can lose water with formation of the corresponding anhydro-bases, I*a* and III*a* respectively.

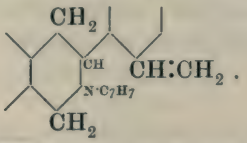


If the reaction proceeds according to the first scheme, the asymmetry of the asymmetric carbon atom is preserved, whereas according to the third scheme it is lost. Since therefore *l*-canadine ethohydroxide gave an optically inactive anhydro-base, the latter is to be formulated as III*a*. This conclusion has since been criticised by McDavid, Perkin, and Robinson (T., 1912, **101**, 1218), who regarded this formula as improbable, since it contains a ten-membered ring, and in order to account for the production by Voss and Gadamer of an optically inactive anhydro-base from optically active *l*-canadine ethohydroxide by heat, suggested that the reactions involved were probably correctly represented in the scheme shown below, which was not further elaborated:



According to this view the reaction does not proceed through the hypothetical carbinol base, but the hydroxyl group attached to the nitrogen atom, together with a hydrogen atom from the asymmetric carbon atom, are together eliminated in the form of water, yielding the anhydro-base X, which then rearranges itself to the anhydro-base I*a*. It may be pointed out that this method of representing the formation of an anhydro-base from its parent quaternary alkyl hydroxide is unusual, and is frankly designed to meet the particular case.

McDavid, Perkin and Robinson themselves actually studied experimentally the degradation of tetrahydroberberine benzyl chloride down to the nitrogen-free compound berberilene. The first step in this series was the conversion of the former compound into the corresponding anhydro-base, which was carried out by boiling with alcoholic potassium hydroxide. To the product, which was isolated in the form of its hydrochloride, they ascribed the constitution of *N*-benzyl*iso*tetrahydroberberine:



The views of Voss and Gadamer on the one hand, and of McDavid, Perkin, and Robinson on the other as to the constitution of their respective anhydro-bases are therefore divergent.

Quite recently, the present author, in collaboration with Jowett (this vol., p. 290), isolated *l*-α-canadine methochloride from *Xanthoxylum Brachyacanthum.* Before the identity of this compound was established a quantity was converted into the corresponding anhydro-base, and evidence was obtained that this was not a simple substance, but a mixture, since its optical activity gradually diminished on repeated crystallisations.

Now Voss and Gadamer had found, as has already been noted, that the crude product obtained by the action of heat on *l*-canadine ethohydroxide was optically active, whilst, after purification, an optically inactive anhydro-base identical with that obtained from tetrahydroberberine ethohydroxide was obtained, and had reserved the further study of this point for a later occasion. As it seemed probable that the study of the effect of heat on the methohydroxide of *l*-canadine would yield valuable information as to the nature of the anhydro-bases produced, Prof. Gadamer was communicated with, and he very kindly expressed his willingness that the present author should continue the work.

The investigation has shown that when *l*-canadine methohydroxide is evaporated to dryness in a vacuum, a mixture of no less than three isomeric anhydro-bases having the composition $C_{21}H_{23}O_4N$ results. The melting points, optical behaviour, and yields in percentages of the theoretical are as follows:

| | M. p. | | Yield, per cent. |
|---|---|---|---|
| Base *A*...... | 135—136° (corr.) | optically inactive | 53 |
| ,, *B*...... | 114—115 ,, | ,, ,, | 4 |
| ,, *C*...... | 101—102 ,, | $[\alpha]_D$ −113·6° | 12 |

The three bases behave as unsaturated compounds towards bromine and permanganate, and each forms a characteristic hydrochloride and methiodide.

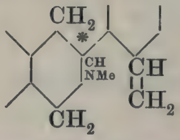
When the corresponding racemic compound, tetrahydroberberine methohydroxide, is similarly treated, the base *A* is obtained in 54 per cent. yield, and the base *B* in 19 per cent. yield. The yield of base *B* in this case is thus approximately equivalent to that of *B* + *C* in the case of *l*-canadine methohydroxide, and this suggests that *B* is the racemic form of *C*.

When, however, *l*-canadine methohydroxide is evaporated to dryness on the water-bath under atmospheric pressure, the base *A* is not found amongst the products of the reactions, but a mixture of *B* and *C* results.

Similarly, when tetrahydroberberine methohydroxide is evaporated to dryness on the water-bath, under atmospheric pressure, the base *A* is not found, and the only anhydro-base obtained is *B*. The yields in the two latter cases are only moderate owing to the neutralisation of a part of the methohydroxide by the carbonic acid of the atmosphere, for the carbonate so formed is not converted into anhydro-base by heating with water on the water-bath. This has been shown definitely by a separate experiment in which a quantity of tetrahydroberberine methohydroxide was saturated with carbonic acid and evaporated on the water-bath; as the evaporation proceeded, crystals of the carbonate separated, and even after concentration to a paste the product was completely soluble in hot water excepting a slight turbidity, and deposited crystals of the carbonate on cooling. The solutions of the carbonates resulting after the removal of the anhydro-bases *B* + *C* or *C* in the experiments described above can be caused to yield further quantities of these bases by the addition of alkali hydroxides which remove the carbonic acid. By this means, a yield of 71 per cent. of *B* and 11 per cent. of *C* has been obtained in the dehydration of *l*-canadine methohydroxide under atmospheric pressure, and a yield of 79 per cent. of *B* from tetrahydroberberine methohydroxide in similar circumstances.

The preparation of the three bases having been described, it now remains to describe their properties and discuss their constitutions.

In the first place, the optically active base *C* can only have the constitution given below:



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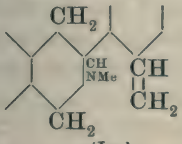
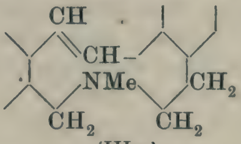
* An asterisk over the asymmetric carbon atom denotes that the compounds are optically active.

Now, a marked difference in behaviour is shown by the base *A* on the one hand, and the bases *B* and *C* on the other. In the first place, the hydrochloride of *A* is readily soluble in boiling water containing a little hydrochloric acid, whilst those of *B* and *C* are very sparingly soluble; secondly, whilst freshly prepared cold aqueous alcoholic solutions of the three bases are only faintly alkaline in their reaction to litmus, after short heating in the water-bath, the solution of *A* becomes very strongly alkaline, whilst the solutions of *B* and *C* are unchanged. Further, as has already been pointed out, when the optically inactive tetrahydroberberine methohydroxide is employed for the preparation of the anhydro-bases in the place of *l*-canadine methohydroxide, an additional quantity of *B* is found in the place of *C*. It follows that *B* is the racemic form of *C*, since there are only two* optically inactive anhydro-bases, namely, I*a* and III*a*, theoretically derivable from tetrahydroberberine methohydroxide, and of these I*a* is the racemic form corresponding with the optically active base *C*. There can be no doubt, therefore, that *B* has the formula I*a*, whilst *A* must then have the formula III*a*.



(I*a*.)



(III*a*.)

The behaviour of *A* with hot aqueous alcohol is entirely similar to that of Voss and Gadamer's anhydroethylcanadine, which, the latter authors showed, became converted into tetrahydroberberine ethohydroxide in similar circumstances. They also showed that the salts of their base underwent a similar change, and represented it according to the schemes shown on p. 822, which depend on the adoption of Willstätter's (*Annalen*, 1903, **326**, 4) and Decker's (*Ber.*, 1904, **37**, 520) methods of representing such a change respectively:

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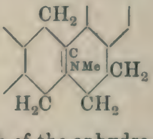
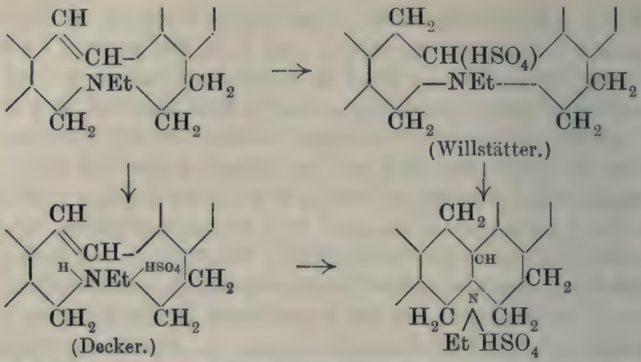
* The possibility that one of the anhydro-bases might have a formula analogous to McDavid, Perkin, and Robinson's intermediate product X (p. 818):



is eliminated by the fact that each of the anhydro-bases forms a distinct unsaturated hydrochloride from which it can be prepared by treatment with ammonia, whereas a base of the above formula could only yield with hydrochloric acid the saturated quaternary salt, tetrahydroberberine methochloride.


(Willstätter.)

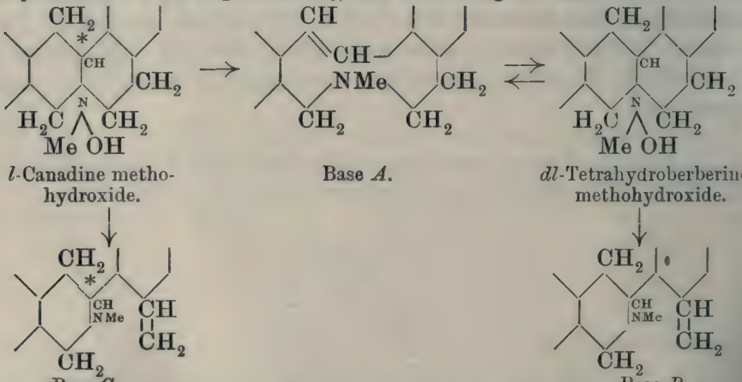
(Decker.)

It has now been found that the change takes place in the case of anhydromethylcanadine base *A* with great readiness. After short boiling with aqueous alcohol, this base is converted into a solution of β-tetrahydroberberine methohydroxide, which, when acidified with hydrochloric acid, yields the corresponding methochloride in a yield amounting to 71 per cent. of the theoretical.

It has already been shown that tetrahydroberberine methohydroxide, when evaporated to dryness under atmospheric pressure, yields the base *B*, and it is consequently not surprising to find that the base *A*, when similarly evaporated several times with dilute alcohol, is converted into a mixture of base *B* and the quaternary carbonates.

The disappearance of base *A* when either *l*-canadine or tetrahydroberberine methohydroxides are evaporated on the water-bath under atmospheric pressure, and the formation of the optically inactive base *B* from *l*-canadine, are thus accounted for.

The whole course of the formation of the three anhydro-bases may therefore be explained by the following scheme:


*l*-Canadine methohydroxide.

Base *A*.

*dl*-Tetrahydroberberine methohydroxide.

Base *C*.

Base *B*.

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* An asterisk over the asymmetric carbon atom denotes that the compounds are optically active.

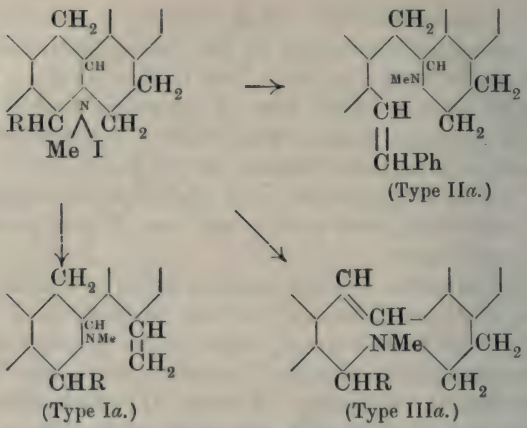
*l*-Canadine methohydroxide, when evaporated either in a vacuum or under atmospheric pressure on the water-bath, yields a small proportion of the optically active base *C* directly; in a vacuum, it yields a large amount of the base *A*, of which a small proportion is converted through tetrahydroberberine methohydroxide into base *B*; under atmospheric pressure, at the water-bath temperature, the whole of *A* is converted into tetrahydroberberine methohydroxide and transformed partly into base *B*, and partly into the quaternary carbonates.

Tetrahydroberberine methohydroxide shows a similar behaviour except that the base *C* cannot be here formed; in a vacuum, a mixture of *A* and *B* is obtained, whilst under atmospheric pressure the only anhydro-base in the final product is *B*. It may be inferred by analogy with the behaviour of *l*-canadine methohydroxide that in the case of tetrahydroberberine methohydroxide a small proportion of base *B* is produced directly in each case.

Applying these results to the work of former investigators, it is clear that Voss and Gadamer's anhydroethylcanadine has, in fact, the constitution which these authors assigned to it. The contention of McDavid, Perkin, and Robinson with respect to its constitution and mode of formation is consequently invalid. The constitution which the latter authors assigned to their anhydro-derivative of tetrahydroberberine benzyl chloride, namely, that of *N*-benzyl-*iso*tetrahydroberberine, is, however, doubtless correct, for the conditions of its formation, namely, boiling with alcoholic potassium hydroxide, were such that even if a base of the type of base *A* were primarily produced, it would be converted into a base of the type of base *B*.

It is interesting to note that while these results were being written up for publication there appeared in the *Chemiker Zeitung* of the 4th of March (1913, **27**, 270) a report of a paper read by M. Freund before the *Chemische Gesellschaft zu Frankfort a.M.*, on the 13th December, 1912, in which the degradation of the α-alkyltetrahydroberberine methiodides is recorded.

The full account of this research has since appeared in the *Annalen* (1913, **397**, 1). It is shown that the degradation of α-alkyl-, arylalkyl-, and aryl-tetrahydroberberine methiodides may take place in different ways:



(Type II*a*.)

(Type I*a*.)

(Type III*a*.)

Where R = benzyl, the anhydro-base was of type II*a*, since it yielded hydrastinine on oxidation.

Where R = *iso*amyl, the main product was an anhydro-base, to which the constitution of the type III*a* was assigned, since it behaved similarly to Voss and Gadamer's anhydroethylcanadine. This base was accompanied by small quantities of an isomeric base of type I*a*, which could also be prepared by boiling the first base with alcohol. The presence of this second base amongst the products of the degradation appears to be regarded as due to transformation of some of the first base by manipulation.

Where R = phenyl or an alkyl radicle other than *iso*amyl, the single anhydro-base isolated was of type I*a*, and the question as to whether this was produced directly or through the intermediate stages of an unstable base of type III*a* changing to the quaternary hydroxide and thence to the isomeride of type I*a*, was left open, although it was pointed out that the latter view more readily accounts for the production of a single anhydro-base from the two stereoisomeric racemic forms of α-alkyltetrahydroberberine hydroxides.

In the light of the present communication it is not surprising that bases of the type of III*a* could not usually be isolated, for the degradation was carried out by boiling with aqueous potassium hydroxide, and it has now been shown that the anhydromethylcanadine of type III*a* is transformed into the base of type I*a* at the temperature of boiling water.

It seems probable that the course of the degradation of the α-alkyltetrahydroberberine methohydroxides is entirely similar to that of tetrahydroberberine methohydroxide as described above, and that a quantitative study of their dehydration in a vacuum would confirm this view.

## EXPERIMENTAL.

### *Tetrahydroberberine Methochlorides.*

The methylation of *l*-canadine (Jowett and Pyman, T., 1913, **103**, 296) gave a mixture of the α- and β-methochlorides, of which the latter more sparingly soluble salt was formed in the larger proportion. An experiment was described, showing that the latter was, in fact, the β-salt, that is, the more stable isomeride. Similarly, the methylation of tetrahydroberberine yields two isomeric salts, of which one, the more sparingly soluble, is formed in the larger proportion; the latter is therefore the racemic form of *l*-β-canadine methochloride.

Twenty-five grams of tetrahydroberberine and 30 c.c. of methyl iodide were heated for fifteen minutes on the water-bath under a reflux condenser; the excess of methyl iodide was then distilled off, and the residue dissolved in 1·2 litres of boiling water. The solution was then thoroughly agitated with an excess of silver chloride, filtered from the silver salts, and evaporated to a volume of about 120 c.c. On cooling, a large quantity of the β-methochloride separated, and this was crystallised from 200 c.c. of hot water, when 15·9 grams of the pure salt were obtained in the first crop. The original mother liquors deposited, after concentration and cooling, a quantity of crude α-salt, which was also purified by crystallisation from water. The two salts were separated without difficulty, and these were eventually obtained, 19·5 grams of the β-methochloride, and 6·5 grams of the α-methochloride, both in a pure state. These yields are respectively 60 and 21 per cent. of the theoretical, so that in all 81 per cent. was obtained in a pure state.

*α-Tetrahydroberberine methochloride* crystallises from water in clusters of colourless, prismatic needles, which contain $2H_2O$, all of which is lost at 100°. The air-dried salt sinters at 140°, and melts and effervesces at 144° (corr.). After drying at 100°, it melts and effervesces at 150° (corr.). It is soluble in about 30 parts of cold water, and very readily so in hot water:

0·2062 * lost 0·0184 at 100°. $H_2O = 8·9$.

0·1622 * gave 0·3538 $CO_2$ and 0·0962 $H_2O$. C = 59·5; H = 6·6.

$C_{21}H_{24}O_4NCl,2H_2O$ requires C = 59·2; H = 6·6; $H_2O$ = 8·5 per cent.

0·1496 † gave 0·3520 $CO_2$ and 0·0888 $H_2O$. C = 64·2; H = 6·6.

$C_{21}H_{24}O_4NCl$ requires C = 64·7; H = 6·2 per cent.

*α-Tetrahydroberberine methiodide* was prepared from the methochloride by double decomposition with potassium iodide and recrystallisation from water. It forms warty clusters, which decompose at 251° (corr.). It is anhydrous, and is sparingly soluble in hot, very sparingly so in cold, water:

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* Air-dried.

† Dried at 100°.

0·1430 gave 0·2742 $CO_2$ and 0·0642 $H_2O$. C=52·3; H=5·0.
$C_{21}H_{24}O_4NI$ requires C=52·4; H=5·0 per cent.

*β-Tetrahydroberberine methochloride* crystallises from water in colourless, well-defined, monoclinic prisms. The air-dried salt shows signs of sintering at about 180°, but does not melt and decompose until 288° (corr.). It contains $3H_2O$, of which two are lost at 100°, and the remaining one at 110—120°. It is soluble in about 80 parts of cold water, but readily so in hot water:

0·3828 * lost 0·0312 at 100—110°. $H_2O$=8·2.
0·3828 * „ 0·0448 „ 110—120°. $H_2O$=11·7.
0·1495 * gave 0·3105 $CO_2$ and 0·0885 $H_2O$. C=56·6; H=6·6.
$C_{21}H_{24}O_4NCl,3H_2O$ requires C=56·8; H=6·8; $2H_2O$=8·5; $3H_2O$=12·2 per cent.
0·1440 † gave 0·3248 $CO_2$ and 0·0890 $H_2O$. C=61·5; H=6·9.
$C_{21}H_{24}O_4NCl,H_2O$ requires C=61·8; H=6·4 per cent.

*β-Tetrahydroberberine methiodide* was prepared from the methochloride by double decomposition with potassium iodide and recrystallisation from water. It forms quadrilateral plates, which decompose at 248° (corr.). It is anhydrous, and is sparingly soluble in hot, very sparingly so in cold, water:

0·1472 gave 0·2804 $CO_2$ and 0·0688 $H_2O$. C=52·0; H=5·2.
$C_{21}H_{24}O_4NI$ requires C=52·4; H=5·0 per cent.

### *Physiological Action of* dl-α- *and β-Tetrahydroberberine Methochlorides.*

These two salts have been tested by Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, in the same manner as *l*-α- and *l*-β-canadine methochlorides (T., 1913, **103**, 294). The physiological activities of the two latter salts were previously found to be as 1 : 12. It has now been found that the ratio of activity of *dl*-α- : *dl*-β-salt is as 1 : 4, and of *l*-α- : *dl*-α- as 1 : 5. From these data, the activities of *d*-α- and *d*-β-canadine methochlorides can be calculated, and the relative activity of the four optically active isomerides is as follows: *l*-α- : *d*-α- : *l*-β- : *d*-β-canadine methochloride as 1 : 9 : 12 : 28.

### *Dehydration of Tetrahydroberberine Methohydroxide by Evaporation under Atmospheric Pressure: Formation of Base* B.

(1) Ten grams of tetrahydroberberine and 15 c.c. of methyl iodide were boiled for fifteen minutes on the water-bath under a

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* Air-dried. † Dried at 100°.

reflux condenser. The crystalline mass was then heated to remove the excess of methyl iodide, and the residual methiodide dissolved in 500 c.c. of boiling water. The solution was agitated with an excess of silver hydroxide until all the iodide was removed from it and filtered from the silver salts. The resulting solution of the methohydroxide was then evaporated to dryness on the water-bath under atmospheric pressure, when the crude base *B* separated as an insoluble, grey varnish. This was collected and crystallised from alcohol. The alcoholic and aqueous mother liquors were then mixed, and again evaporated to dryness under the same conditions, when a further quantity of the base was obtained. In this way 5·0 grams of base *B*, melting at 111—112°, were obtained. The combined aqueous and alcoholic mother liquors, which no longer gave a separation of insoluble matter on evaporation, were extracted with chloroform, which, however, removed only a trace of material. The liquor was then acidified with hydrochloric acid, when considerable effervescence took place, and 3·2 grams of β-tetrahydroberberine methochloride separated.

(2) It seemed clear from the last experiment that the cause of the low yield of the anhydro-base lay in the combination of a part of the methohydroxide with the carbonic acid of the atmosphere, and this was proved by the following experiment.

Five grams of tetrahydroberberine were converted into a solution of the methohydroxide in 240 c.c. of water in the usual manner, and this solution was then saturated with carbonic acid and evaporated to low bulk. No insoluble, amorphous matter separated during concentration, but a quantity of crystals were obtained in its place, and even after evaporation of the liquor to a thick paste, no insoluble anhydro-base separated. The liquor was then somewhat diluted and set aside to crystallise, the crystals so obtained being again recrystallised from water, when they were found to consist of β-tetrahydroberberine methocarbonate (1·8 grams):

0·1532 * lost 0·0237 at 100°. $H_2O = 15·5$.

$C_{22}H_{25}O_7N,4H_2O$ requires $H_2O = 14·8$ per cent.

0·1228 † gave 0·2849 $CO_2$ and 0·0702 $H_2O$. $C = 63·3$; $H = 6·4$.

$C_{22}H_{25}O_7N$ requires $C = 63·6$; $H = 6·1$ per cent.

This salt, after drying at 100°, melts and effervesces at 165—167° (corr.); it is readily soluble in hot, sparingly so in cold, water. The mother liquors from this salt, on evaporation to dryness with the addition of potassium hydroxide, readily furnished 1·6 grams of base *B*, melting at 112—113°.

(3) Tetrahydroberberine (25 grams) was then converted into a solution of methohydroxide, just as in the first experiment, but

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* Air-dried.

† Dried at 100°.

when the aqueous mother liquors no longer gave a separation of insoluble material on evaporation, potassium hydroxide was added, and a further quantity of the anhydro-base was obtained. Under these conditions 15·7 grams of base *B*, melting at 111—112°, and 4·8 grams, melting at 110—111°, were obtained, the total quantity, 20·5 grams, representing 79 per cent. of the theoretical.

### *Dehydration of Tetrahydroberberine Methohydroxide by Evaporation in a Vacuum: Formation of Bases* A *and* B.

Twenty-five grams of tetrahydroberberine were converted into a solution of the methohydroxide in 1200 c.c. of water, as in the preceding example. This was evaporated to dryness under the diminished pressure effected by a good water-pump, the bolt-head containing the solution being placed in a vigorously boiling water-bath. The product was heated under these conditions for a further thirty minutes after it appeared to be dry. The residue was then boiled with 100 c.c. of ethyl acetate, which had been well dried over anhydrous potassium carbonate, and filtered from a very small amount of insoluble matter. The filtrate deposited, on cooling, a large quantity of the base *A* in colourless, silky needles, melting at 132—133°; the mother liquor from these, on concentration to about half volume and cooling, gave a further crop of the same melting point. The two crops together amounted to 13·0 grams. The ultimate mother liquor was evaporated to dryness, and the residual mixture of bases separated by means of the different solubilities of the hydrochlorides.

The residue was ground with 100 c.c. of hot 3 per cent. aqueous hydrochloric acid, which separated the mixture into hydrochlorides easily soluble, and nearly insoluble in hot dilute hydrochloric acid. The acid solution was filtered from the insoluble hydrochlorides, and the latter well washed with hot aqueous 1 per cent. hydrochloric acid; the filtrate and washings were then combined, rendered alkaline with ammonia, and extracted with ether. The ethereal solution, after being dried and distilled to a volume of a few c.c., deposited on cooling 1·1 grams of base *A*, melting at 132—133°, whilst the filtrate from these crystals gave, on evaporation to dryness, 0·9 gram of partly crystalline material. The total yield of base *A*, 14·1 grams, is 54 per cent. of the theoretical.

The insoluble hydrochlorides were shaken with ammonia and ether, and the ethereal solution was evaporated to dryness and dissolved in a little alcohol. On keeping, 5·0 grams of base *B*, melting at 111—112°, were collected, and the mother liquor contained only 0·3 gram of amorphous substances.

The yield of base *B*, 5·0 grams, is 19 per cent. of the theoretical.

### *Dehydration of* l-*Canadine Methohydroxide by Evaporation under Atmospheric Pressure: Formation of Bases* B *and* C.

(1) Ten grams of *l*-canadine were converted into a solution of the methohydroxides in water in the usual manner.* This solution, amounting in volume to about 500 c.c., was evaporated to dryness on the water-bath under atmospheric pressure; the residue was diluted with water, and the separated clear, grey varnish crystallised from a quantity of alcohol just sufficient to dissolve it when hot; on cooling, the first crop of crystals separated. The aqueous and alcoholic mother liquors were then combined, again evaporated to dryness, and subjected to the same treatment once more, yielding the second crop of crystals. The aqueous and alcoholic mother liquors from the second crop were then combined and again evaporated to dryness when very little insoluble matter separated, since the compound was now present in the form of methyl carbonate owing to combination with the carbonic acid of the atmosphere. A quantity of 10 per cent. aqueous potassium hydroxide was added, and evaporation to low bulk was repeated twice, when a further quantity of base insoluble in water was formed. After crystallisation from a little alcohol, this formed the third crop.

The amounts and properties of the three crops were as follows:

| | Grams. | M. p. | $[\alpha]_D$. |
|---|---|---|---|
| 1st crop ........... | 3·3 | 105—110° | −41·9° |
| 2nd ,, ........... | 1·5 | 108—111 | −19·8 |
| 3rd ,, ........... | 2·7 | 111—113 | − 3·8 |

Fractional crystallisation from ethyl acetate of these crops, together with those of the second experiment described below, gradually effected a separation into substances of low and high rotation, the latter being more readily soluble. After repeated crystallisations, the most sparingly soluble fraction was obtained almost free from optical activity ($[\alpha]_D$ $-0·3°$), when it melted at 114—115° (corr.), and was found to represent the base *B* in a nearly pure state:

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* The mixture of α- and β-methohydroxides obtained in this way was always employed for the dehydration. The possibility that the two compounds might behave differently had been tested in the preliminary experiments in the case of evaporation on the water-bath (this vol., p. 299). It was there stated that 10 grams of *l*-α-canadine methiodide gave 4·1 grams of anhydro-base, melting at 111—112°, and having $[\alpha]_D$ −25·2° (after one crystallisation from alcohol). This yield is 56 per cent. of the theoretical. It was further stated that a similar result was obtained, starting from *l*-β-canadine methochloride; the details of the latter case are as follows:

Eight grams of hydrated *l*-β-canadine methochloride gave 2·8 grams of anhydro-base, melting at 111—112°, and having $[\alpha]_D$ −24·0° (after one crystallisation from alcohol). This yield is 49 per cent. of the theoretical.

The anhydro-base obtained in these experiments was, of course, a mixture of the anhydro-bases *B* and *C*; the above results indicate that they are produced in approximately the same proportion, whether the α- or β-metho-salts are employed.

0·1526 gave 0·3994 $CO_2$ and 0·0890 $H_2O$. C=71·4; H=6·5.
$C_{21}H_{23}O_4N$ requires C=71·4; H=6·6 per cent.

The purification of the more readily soluble portion was more difficult, and the quantity of material was insufficient to admit of complete purification, but an end-fraction, melting at 99—101° and having $[\alpha]_D$ $-99°$, was obtained, consisting mainly of base *C*, which it is subsequently shown melts at 101—102° (corr.), and has $[\alpha]_D$ $-113·6°$ when pure. No evidence of the presence of a third constituent of the mixture was obtained, and it is therefore admissible to calculate the proportion of two bases in the mixture from the known specific rotations of *B* and *C*.

The yields thus calculated are 57 per cent. of the theoretical of *B*, and 15 per cent. of *C*.

(2) Twenty-five grams of *l*-canadine were then converted into the methohydroxide, but in order to avoid contact with the carbonic acid of the atmosphere as far as possible, the solution was evaporated on the water-bath in a vacuum to a volume of about 200 c.c. It was then transferred to an evaporating dish, the small amount of base that had separated on the sides of the vessel being washed in with a little alcohol, and the evaporation to dryness continued under atmospheric pressure. The resulting product was then treated as in the previous case, two crops being collected before, and one after, the addition of potassium hydroxide. They were:

| | Grams. | M. p. | $[\alpha]_D$. |
|---|---|---|---|
| 1st crop ............ | 16·6 | 109—111° | −22° |
| 2nd ,, ............ | 1·5 | 106—110 | −33 |
| 3rd ,, ............ | 4·2 | 111—112 | − 8 |

The yields of the two bases calculated from these figures are: Base *B*, 71 per cent. of the theoretical; base *C*, 11 per cent. of the theoretical.

### *Dehydration of* l-*Canadine Methohydroxide by Evaporation in a Vacuum: Formation of Bases* A, B, *and* C.

Thirty grams of *l*-canadine were converted into a solution of the methohydroxide in 1500 c.c. of boiling water in the usual manner. The solution was then evaporated to dryness under the diminished pressure effected by a good water-pump, the bolt-head containing the solution being placed in a vigorously boiling water-bath, and the residue was heated under these conditions for a further thirty minutes after it appeared to be dry.

The residue was then boiled with about 100 c.c. of ethyl acetate, which had been well dried over anhydrous potassium carbonate, and filtered from a very small amount of insoluble matter. The filtrate, on cooling, deposited a large quantity of the base *A* in colourless, silky needles, melting at 133°; the mother liquor from these, on concentration to about half volume and cooling, gave a further crop, melting at 131°. The two crops together amounted to 14·8 grams.

The ultimate ethyl acetate mother liquor, after concentration to very low bulk, gave about 8 grams of a mixture of bases, melting at 85—95°, and a residue of 2·5 grams of gummy bases.

These last two fractions were ground with 100 c.c. hot 3 per cent. aqueous hydrochloric acid, which separated the mixture into hydrochlorides soluble and nearly insoluble in hot dilute hydrochloric acid.

The acid solution was filtered from the insoluble hydrochlorides, and the latter well washed with hot very dilute hydrochloric acid; the filtrate and washings were then combined, rendered alkaline with ammonia, and extracted with ether. The ethereal solution, after being dried and distilled to a volume of a few c.c., deposited, on cooling, 1·9 grams of the base *A*, melting at 133°, the filtrate from this on evaporation to dryness amounting to only 0·8 gram of partly crystalline material.

The total yield of the nearly pure base *A* thus amounts to 16·7 grams, that is, 53 per cent. of the theoretical.

The insoluble hydrochlorides were shaken with ammonia and ether, and the ethereal solution was evaporated to low bulk and kept, when crystals separated; the mother liquor, on concentration, deposited a further quantity of crystals, and eventually the following fractions were obtained in the order given:

| Grams. | M. p. | $[\alpha]_D$. |
|---|---|---|
| 3·0 | 105° | − 72° |
| 1·5 | 102 | − 98 |
| 0·6 | 98 | − 101 |
| 0·2 | residue | |

In a second experiment, using 50 grams of *l*-canadine, the similar fractions obtained were:

| Grams. | M. p. | $[\alpha]_D$. |
|---|---|---|
| 5·7 | 102—106° | − 60° |
| 3·9 | 100—102 | − 83 |

The fractions from these two experiments and from a preliminary experiment, in all 18·9 grams, with specific rotatory power from

$-30°$ to $-101°$, were suitably combined, and crystallised fractionally from ethyl acetate. By this means a gradual separation was effected, and at a certain stage, for instance, 8·0 grams, melting at 111—113° and having $[\alpha]_D -18·6°$, were obtained as the most sparingly soluble portion, and 5·7 grams in small fractions, melting at about 100° and having $[\alpha]_D$ from $-103°$ to $-108°$ as the most readily soluble portion.

The first of these fractions after two crystallisations from 25 c.c. of alcohol amounted to 4·3 grams with $[\alpha]_D -11·3°$, and after two further crystallisations from ethyl acetate to 2·0 grams with $[\alpha]_D -2·4°$; after two further crystallisations from ethyl acetate, 0·6 gram with $[\alpha]_D -2·3°$ was obtained. In spite of the constancy obtained in the specific rotatory power, there is little reason to doubt that this more sparingly soluble fraction consists mainly of the inactive base *B*. It melted at the same temperature, namely, 114—115° (corr.), did not depress the melting point of the latter, and had the same general properties.

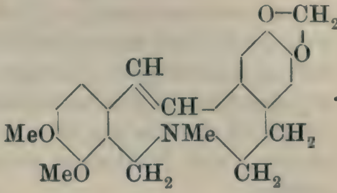
The later fraction, which was readily soluble in cold ethyl acetate, was crystallised from a mixture of this solvent (1 part) with alcohol (3 parts), when fractions of somewhat lower rotation separated at first; on concentrating the mother liquors and cooling, fractions of higher rotation crystallised. The latter were crystallised in a similar manner, until of almost constant specific rotatory power, and eventually furnished a small quantity of the base *C* with $[\alpha]_D -113·6°$.

Whilst this product is regarded as very nearly pure, it must be pointed out that the purification of a substance which tends to remain in the mother liquors is necessarily difficult, and it may be that a repetition of this experiment with still larger quantities might result in the isolation of base *C* with a slightly higher specific rotatory power.

No evidence was obtained during the fractionation of the presence of a constituent other than *B* or *C*, and it is therefore admissible to calculate the proportion of the two bases in the original mixture, assuming that *B* is optically inactive, and that *C* has $[\alpha]_D -113·6°$.

It is thus found that the crystalline fractions from the first experiment, 5·1 grams, amounted to 1·4 grams of *B*, that is, 4 per cent., and 3·7 grams of *C*, that is, 12 per cent. of the theoretical; whilst in the second experiment the total quantity (8·6 grams) represents 2·8 grams of *B*, that is, 5 per cent., and 5·8 grams of *C*, that is, 11 per cent. of the theoretical.

*Anhydromethylcanadine* (*Base* A).



This base is the chief product of the dehydration of *l*-canadine and tetrahydroberberine methohydroxide by evaporation to dryness in a vacuum, and is formed in a yield amounting to about 53 per cent. of the theoretical. It crystallises from anhydrous ethyl acetate in colourless, woolly needles, which melt at 135—136° (corr.). It suffers no loss at 100°, and is optically inactive:

0·1556 gave 0·4058 $CO_2$ and 0·0920 $H_2O$. C = 71·1; H = 6·6.
0·1676 „ 0·4370 $CO_2$ „ 0·0994 $H_2O$. C = 71·1; H = 6·6.
$C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·6 per cent.

Molecular-weight determination by the cryoscopic method:
0·2096 in 18·56 benzene gave $\Delta t$ $-0·170°$. M.W. = 332.
0·5624 „ 18·56 „ „ $\Delta t$ $-0·440°$. M.W. = 352.
$C_{21}H_{23}O_4N$ requires M.W. = 353.

It is insoluble in water, sparingly soluble in cold alcohol, ethyl acetate, or ether, and readily so in chloroform or hot ethyl acetate. It is decomposed by hot alcohol. The cold alcoholic solution reacts faintly alkaline to litmus, but after heating this solution for a few minutes on the water-bath, the solution reacts strongly alkaline owing to the formation of tetrahydroberberine methohydroxide. The readiness with which this conversion takes place is illustrated by the following experiment.

Three grams of the pure base were dissolved in 30 c.c. of hot alcohol, and 30 c.c. of water were added; the alcohol was then distilled from the solution, leaving it slightly turbid. A further quantity of 10 c.c. of alcohol, followed by 20 c.c. of water, was next added, and the alcohol again removed by distillation. The solution was then filtered from a very small quantity of insoluble amorphous matter, and acidified with concentrated hydrochloric acid. On cooling, 2·8 grams of β-tetrahydroberberine methochloride separated in a pure state, that is, 71 per cent. of the theoretical yield. This salt was identified as such by its melting point, crystalline form, sparing solubility in water, and inability to decolorise potassium permanganate. The mother liquor from this salt did not appear to contain any of the α-methochloride.

Anhydromethylcanadine (Base *A*) is also decomposed on heating with chloroform. A solution of 1 gram in 25 c.c. of chloroform was evaporated to a syrup and kept, when the residue set to a crystalline mass having a high melting point. After extracting this with a little hot water, the filtered extract deposited crystals, which were again recrystallised from water, and then represented 0·6 gram of pure β-tetrahydroberberine methochloride.

Base *A* decolorises bromine in chloroform, yielding a colourless solution, and decolorises potassium permanganate in aqueous acid solution.

The *hydrochloride* of base *A* was obtained as follows:

Two grams of the base were added to 10 c.c. of hot 5 per cent. hydrochloric acid, and the solution cooled, when the aqueous salt separated in rosettes of colourless plates. This salt sintered somewhat at 150—155° (corr.), but did not melt until 288° (corr.), being probably converted into β-tetrahydroberberine methochloride under the influence of heat:

0·1760 * lost 0·0176 at 100°. $H_2O = 10·0$.
0·1472 † „ 0·3356 $CO_2$ and 0·0860 $H_2O$. $C = 62·2$; $H = 6·5$.
$C_{21}H_{23}O_4N,HCl,3\frac{1}{2}H_2O$ requires loss of $2\frac{1}{2}H_2O = 9·9$ per cent.
$C_{21}H_{23}O_4N,HCl,H_2O$ requires $C = 61·8$; $H = 6·4$ per cent.

This salt is readily soluble in hot, sparingly so in cold, water. Freshly made solutions of this salt in water gave with ammonia a white precipitate, at first amorphous, then crystalline, of the original base *A*, and decolorised aqueous potassium permanganate. An aqueous solution of the salt, after digestion for a short time in the water-bath, no longer gave a turbidity with ammonia nor decolorised potassium permanganate, owing to the conversion of the salt into β-tetrahydroberberine methochloride.

The *methiodide* of base *A* was prepared by heating the latter with methyl iodide for a few minutes on the water-bath. It crystallises from alcohol in colourless plates containing EtOH, which begin to turn brown at about 220°, and to sinter and effervesce at 225° (corr.). It is sparingly soluble in cold water or alcohol, but fairly readily so in hot water. It decolorises potassium permanganate in aqueous solution:

0·1721 lost 0·0045 at 120°. EtOH = 2·6.
0·1676 ‡ gave 0·3276 $CO_2$ and 0·0848 $H_2O$. $C = 53·3$; $H = 5·7$.
$C_{22}H_{26}O_4NI$ requires $C = 53·1$; $H = 5·3$ per cent.

*Conversion of Base* A *into Base* B.—Since the base *A* is easily converted into tetrahydroberberine methohydroxide, and this readily yields the base *B* on evaporation under atmospheric pressure, the conversion of base *A* into base *B* can be readily effected.

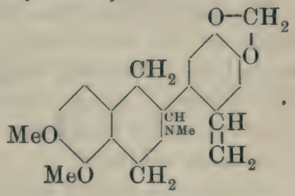
Two grams of base *A* were dissolved in 10 c.c. of hot alcohol, and 10 c.c. of water added. The liquor was evaporated nearly to dryness

* Air-dried. † Dried at 100°. ‡ Dried at 120°.

on the water-bath under atmospheric pressure, and the residue again dissolved in a little alcohol, diluted with water, and again evaporated to dryness. The residue was then mixed with a little hot water, and the insoluble varnish collected and crystallised from alcohol, when 0·75 gram of base *B*, melting at 111—112°, was obtained.

### *Anhydromethylcanadine* (*Base* B).

dl-N-*Methyl*iso*tetrahydroberberine*,



This base is the sole anhydro-base produced by the evaporation of an aqueous solution of tetrahydroberberine methohydroxide under atmospheric pressure, the yield amounting to 79 per cent. of the theoretical, when potassium hydroxide is employed to decompose the methocarbonates formed at the same time. It is also formed in 19 per cent. yield, when the same compound is evaporated in a vacuum, and is further obtained mixed with the lævo-variety by the degradation of *l*-canadine methohydroxide. This base crystallises from alcohol in tufts of small, colourless needles, which melt at 114—115° (corr.). It is anhydrous, and is insoluble in water, sparingly soluble in cold, but readily so in hot, alcohol, fairly readily soluble in cold, and very readily so in hot, ethyl acetate, fairly readily soluble in ether, and readily so in chloroform:

0·1598 gave 0·4183 $CO_2$ and 0·0940 $H_2O$. $C=71·4$; $H=6·6$.

$C_{21}H_{23}O_4N$ requires $C=71·4$; $H=6·6$ per cent.

Molecular-weight determination by the ebullioscopic method:

0·1824, in 23·28 chloroform, gave $\Delta t$ 0·072°. M.W. = 398.
0·4012, „ 23·28 „ „ $\Delta t$ 0·185°. M.W. = 341.
0·4978, „ 23·28 „ „ $\Delta t$ 0·243°. M.W. = 322.

$C_{21}H_{23}O_4N$ requires M.W. = 353.

This base is optically inactive. An alcoholic solution reacts faintly alkaline to moist litmus paper, and does not become more alkaline after boiling on the water-bath. It decolorises bromine in chloroform, yielding a nearly colourless solution with a faint green tinge, and decolorises potassium permanganate in aqueous acid solution. This base and its salts are not converted into tetrahydroberberine methohydroxide and metho-salts in the various circumstances in which base *A* and its salts are so converted.

The *hydrochloride* was prepared by adding dilute aqueous hydrochloric acid to an alcoholic solution of the base, when it separated in white, matted, woolly needles, which decompose at 258° (corr.). It is anhydrous, and is very sparingly soluble in cold water or alcohol, more readily so in these solvents when hot. It is very sparingly soluble in hot dilute hydrochloric acid:

0·1468 gave 0·3470 $CO_2$ and 0·0778 $H_2O$. C = 64·4; H = 5·9.

$C_{21}H_{23}O_4N,HCl$ requires C = 64·7; H = 6·2 per cent.

The *methiodide* was prepared by heating the base with methyl iodide on the water-bath for a few minutes. It crystallised from alcohol in colourless, anhydrous plates, which melted sharply at 231° (corr.). It is very sparingly soluble in cold, more readily so in hot, water or alcohol. It decolorises potassium permanganate in aqueous solution:

0·1820 gave 0·3562 $CO_2$ and 0·0852 $H_2O$. C = 53·4; H = 5·2.

$C_{22}H_{26}O_4N$ requires C = 53·3; H = 5·3 per cent.

### *Anhydromethylcanadine* (*Base* C).

### 1-N-*Methyl*iso*tetrahydroberberine.*

This base is produced in a yield of about 12 per cent. by the dehydration of *l*-canadine methohydroxide either under atmospheric pressure or in a vacuum. It crystallises from alcohol in clusters of clear, colourless prisms, which melt at 101—102° (corr.). It is anhydrous and is insoluble in water, somewhat sparingly soluble in cold, but readily so in hot, alcohol, readily soluble in cold, and very readily so in hot, ethyl acetate, and readily soluble in ether or chloroform:

0·1517 gave 0·3986 $CO_2$ and 0·0913 $H_2O$. C = 71·6; H = 6·7.

$C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·6 per cent.

The specific rotatory power was determined in chloroform solution:

$$\alpha_D\ -2{\cdot}30°;\ c = 1{\cdot}012;\ l = 2\ \text{dcm.};\ [\alpha]_D\ -113{\cdot}6°.$$

An alcoholic solution reacts faintly alkaline to moist litmus paper, and does not become more alkaline after boiling on the water-bath. It decolorises bromine in chloroform, yielding a nearly colourless solution with a faint green tinge, and decolorises potassium permanganate in aqueous acid solution. This base and its salts are not converted into tetrahydroberberine methohydroxide and metho-salts in the various circumstances in which base *A* and its salts are so converted.

The *hydrochloride* was prepared in the same manner as the salt of the racemic base. It separated in tufts of woolly needles, which melted at 229° (corr.). It is very sparingly soluble in cold water, sparingly so in hot water or cold alcohol, and fairly readily so in hot alcohol. It is very sparingly soluble in hot dilute hydrochloric acid:

0·1497 gave 0·3565 $CO_2$ and 0·0836 $H_2O$. C = 64·9; H = 6·2.
$C_{21}H_{23}O_4N,HCl$ requires C = 64·7; H = 6·2 per cent.

The *methiodide* crystallises from alcohol in colourless plates, which melt at 230° (corr.). It is anhydrous, and is sparingly soluble in cold water or alcohol. It decolorises potassium permanganate in aqueous solution:

0·1687 gave 0·3310 $CO_2$ and 0·0805 $H_2O$. C = 53·5; H = 5·3.
$C_{22}H_{26}O_4NI$ requires C = 53·4; H = 5·3 per cent.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

# LXXXV.—*Optical Activity and Enantiomorphism of Molecular and Crystal Structure.*

By THOMAS VIPOND BARKER and JAMES ERNEST MARSH.

THE view may be regarded as axiomatic that the property of optical activity is wholly restricted to substances possessing an enantiomorphous structure, that is, a structure which is non-superposable with its mirror image. It is convenient to divide optically active substances into two classes: first, those in which the rotatory power is limited to the crystalline state of aggregation, as, for example, quartz; secondly, those in which the activity persists when the crystalline structure is destroyed by dissolving, liquefying, or vaporising the substance, for example, seignette salt, camphor, and turpentine. The prevailing view concerning these two classes is that in the first the seat of the activity lies in an enantiomorphous, spiral grouping of the molecules in the crystal edifice, which breaks down on dissolution, whilst in the second class the activity is referred to an enantiomorphous configuration of the atoms within the chemical molecule, which configuration is independent of the state of aggregation.

The objects of the present paper are: first, to point out that the theory of crystal structure is incapable of accounting for the activity of many substances of the first class by a spiral grouping of molecules, from which it follows that the molecular configuration must be enantiomorphous in the same sense as is recognised for substances of the second class; secondly, to indicate for such substances chemical constitutions of an enantiomorphous character which seem to be in harmony with the general chemical behaviour of the substances concerned.

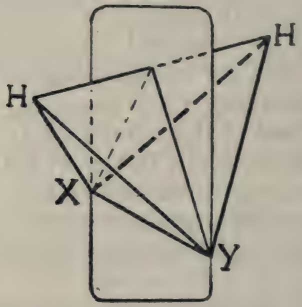
Before proceeding to the main theme it will be necessary to discuss separately the general nature of molecular and crystal structure which shall exhibit enantiomorphism.

### *Conditions Necessary for Optical Activity of Molecular Structure.*

In the simpler carbon compounds the essential difference between an enantiomorphous configuration and one which is superposable with its mirror image is that the latter possesses a plane of symmetry, for example, $CH_2XY$ possesses a plane of symmetry, whereas CHXYZ does not, and is, in fact, enantiomorphous. In view of the enormous number of compounds of these types which have been investigated, it is not surprising that chemists came to the conclusion that any structure devoid of a plane of symmetry is necessarily enantiomorphous. This is erroneous. The complete conditions for geometrical enantiomorphism have been long recognised by crystallographers, and are three in number: the molecular configuration must not only be devoid of (1) a plane of symmetry, but also (2) of a centre of symmetry, and (3) of an alternating axis of symmetry. The presence of any one of these three elements of symmetry suffices to render a configuration superposable with its mirror image. The precise meanings of these three terms will now be explained and illustrated by concrete examples.

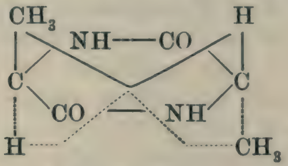
*Plane of Symmetry.*—When a configuration can be divided into two halves so that the reflection of one half across a mirror, placed in contact with the plane of the section, restores the missing half, there is a plane of symmetry. Thus, in a disubstituted product of methane, $CH_2XY$, there is a plane of symmetry cutting the C, X, and Y atoms into equal halves, and each hydrogen atom is symmetrically

FIG. 1

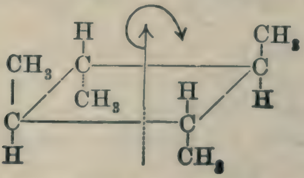


disposed on opposite sides of the plane. Although containing no other symmetry, the substance is superposable with its mirror image, and therefore is incapable of existence in optically active forms.

*Centre of Symmetry.*—This involves similarity about the centre of the molecule in the following sense: lines drawn through the centre of the whole molecule to each and every atom meet a similar atom when produced in the opposite direction. Thus, in *trans*-1 : 4-diketo-2 : 5-dimethylpiperazine (alanyl anhydride) any line drawn through the centre of the ring to any atom (either above, below, or in the ring) meets a similar atom similarly environed, when produced backwards. In the figure given, lines have been drawn connecting pairs of *trans*-hydrogen atoms and methyl groups to indicate the symmetry about the centre ("centrosymmetry") by the presence of which optical activity is precluded (E. Fischer, *Ber.*, 1906, **39**, 467, 3981).



*Alternating Axis of Symmetry.*—This peculiar element of symmetry is illustrated by, say, 1 : 3-*cis*-2 : 4-*trans*-tetramethyl*cyclo*butane. If any hydrogen atom or methyl group be rotated through an angle of 90° about the vertical axis indicated, and then reflected across the horizontal plane (that is, the plane perpendicular to the axis of rotation), it comes into superposition with a corresponding hydrogen atom or methyl group, and the same is true of the molecule as a whole. The similar atoms or groups are seen to alternate successively above and below the plane of reflection; hence the term alternating. The molecule is superposable with its mirror image by virtue of the alternating axis of symmetry.

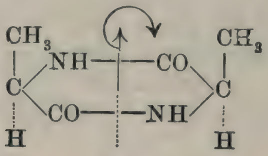


In the illustration just given there are evidently two vertical planes of symmetry cutting diagonally through the ring carbon atoms, and it might be objected that the presence of these two planes of symmetry are in reality the cause of the superposability. If, however, the methyl groups be replaced alternately by the groups CXYZ and CXZY, there would be no longer any planes of symmetry, and the molecule, although possessing no less than eight asymmetric carbon atoms, would be an inactive, internally compensated compound by virtue of the alternating axis of symmetry, which would, in fact, be the sole element of symmetry.

In configurations possessing alternating axes of symmetry, the successive rotations must be 360°/$n$, where $n$ is an even number. When $n=2$, the alternating axis is equivalent to a centre of symmetry; where $n=6$, 10, 14, etc., the alternating axis also involves a centre of symmetry, but where $n=4$ (as above), 8, 12, etc., this does not hold.

In testing a new configuration as to the elements of symmetry actually present, it must be understood that in the case of single linkings the atoms or groups must be rotated into as symmetrical positions as possible, since experience has proved that atoms or groups invariably take up such a symmetrical, favourable configuration by virtue of free rotations about single linkings.

Although an enantiomorphous configuration must be devoid of all the three elements discussed, it need not necessarily be totally devoid of symmetry, that is, asymmetric in the literal sense. For example, the *cis*-form of 1:4-diketo-2:5-dimethylpiperazine, although optically active, possesses an ordinary (as opposed to alternating) axis of symmetry. It is seen that by simply rotating the whole molecule through 180° about the axis indicated, each atom comes into congruence with a similar atom, and the molecule as a whole presents the same aspect before and after the rotation. The above axis is termed digonal, because the rotation is 360°/2. Substances can be easily formulated exhibiting trigonal (rotation = 360°/3), tetragonal, pentagonal, etc., axes of symmetry, of an enantiomorphous character.



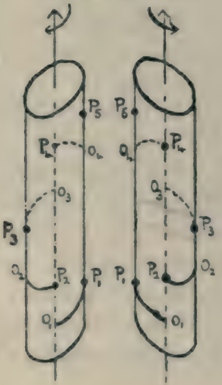
It is almost needless to add that in every case where the constitution of a substance, exhibiting optical activity in the non-crystalline condition, has been established, the molecular configuration is devoid of plane, centre, and alternating axis of symmetry. For example, the two optically active forms of tartaric acid are configurationally devoid of all symmetry whatsoever. The internally compensated meso-form has either a plane of symmetry or a centre of symmetry, according as to which of the two possible favourable configurations is taken up by the molecule by virtue of the free rotation about the single bond between the two central carbon atoms.

### *Conditions Necessary for Optical Activity in the Crystal.*

The optical activity of a crystal may be theoretically due to two causes: first, an enantiomorphous configuration of the molecule, for example, in crystals of tartaric acid and sucrose; secondly, an enantiomorphous, spiral grouping of non-enantiomorphous molecules, for example, in crystals of quartz and cinnabar.

Now, with substances of the second class, the theory of crystal structure demands that the arrangement of molecules must possess "screw axes of symmetry." Suppose points (each representing the mean position of a molecule) be distributed on the surface of a cylinder so that a point $P_2$ is obtained from $P_1$ by the following operations. First rotate $P_1$ through 90° clockwise about the axis of the cylinder to the point $O_1$, then translate $O_1$ any given distance parallel to the cylinder axis to $P_2$. Treating $P_2$ in the same way, points $P_3$, $P_4$ (at the back of the cylinder), $P_5$, etc., are located. It is obvious that $P_5$ lies vertically above $P_1$; further, all the points lie on a spiral. By effecting the rotation in the opposite direction (counter clockwise), but carrying out the translations in the same direction as previously, a spiral enantiomorphous with the former is obtained. When an arrangement of points is of such a nature as the one outlined, it is said to possess screw axes of symmetry.

FIG. 2.



Now in a crystal the angle of rotation may not only be 90°, that is, 360°/4, but also 360°/2, 360°/3, and 360°/6; any other values but these are inadmissible, since they would contravene the fundamental law of geometrical crystallography. The screw axes mentioned are known respectively as tetragonal, digonal, trigonal, and hexagonal.

The character of the digonal screw axis is especially important for the present subject. By a rotation of the point $P_1$ through 180°, followed by a translation equal to half $P_1P_5$, the point $P_3$ is located, and a subsequent operation discovers the point $P_5$. Now the points $P_3$ and $P_5$ are successively obtained, no matter in which direction the rotation is effected; there is no physical difference, then, between a rotation of $+180°$ and one of $-180°$, and the two arrangements are no longer distinguishable by an enantiomorphous, spiral nature. Any assemblage of points possessing no other screw axes save digonal can only be endowed with optical activity providing the points themselves (that is, the molecules) are enantiomorphous.

Crystals belonging to the rhombic, monoclinic, and triclinic systems cannot possess screw axes other than digonal. Again, in the sodium chlorate class of the cubic system, although the point-assemblages exhibit trigonal screw axes, the latter are always paired, each *d*-spiral being accompanied by a *l*-spiral axis. Now optical activity has been recorded in three rhombic, three monoclinic, and four substances having the symmetry of sodium chlorate. Among these ten cases there are four which admittedly have an enantiomorphous molecular configuration, namely, seignette salt, sucrose, rhamnose, and tartaric acid. The remaining six substances, which must equally possess enantiomorphous configurations, are: magnesium sulphate, $MgSO_4,7H_2O$; sodium dihydrogen phosphate, $NaH_2PO_4,H_2O$; Schlippe's salt, $Na_3SbS_4,9H_2O$; sodium uranyl acetate, $NaUO_2(C_2H_3O_2)_3$; sodium chlorate and sodium bromate.

## *Co-ordination and Valency.*

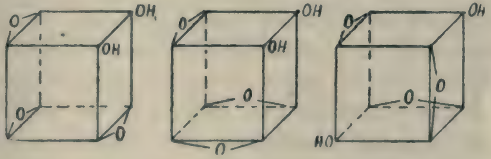
The work of Werner and the views expressed by him on his theory of co-ordination seem to show that whilst the co-ordination number of an element is not the same as its valency, yet, like valency, it is constant for a large series of compounds, and the atoms or groups associated in co-ordination with the element have themselves a monad or dyad character. Thus, the groups Cl, $NO_2$, OH, $NH_3$, $H_2O$ are monad, whilst the groups $C_2H_4(NH_2)_2$, $CO_3$, $C_2O_4$ are dyad. In this way the co-ordination number for cobalt is six, no matter whether it be associated with six $NH_3$-groups or with three ethylenediamine groups. It seems therefore likely that the oxygen atom will have double the co-ordination value of that of chlorine, hydroxyl, or $NO_2$, just as it has double the valency value. It will follow therefore that in the groups $(ClO_3)'$, $(NO_3)'$, $(CO_3)''$, the co-ordination number of Cl, N, and C will be six, and the co-ordination figure will be an octahedron, each oxygen atom being represented as attached to two adjacent corners of the octahedron. Again, in the groups $OsO_4$, $(ClO_4)'$, $(SO_4)''$, $(PO_4)'''$, $(SiO_4)''''$, the co-ordination number will be eight, and the co-ordination figure a cube, where each oxygen atom influences, or is attached to, two adjacent corners.

### *Constitution of Substances with Co-ordination Number Eight.*

To this category belong all the substances previously mentioned excepting sodium chlorate and bromate. The constitutions suggested will be best illustrated by treating the heptahydrated magnesium sulphate in some detail.

*Magnesium Sulphate*, $MgSO_4,7H_2O$.—This salt loses six molecules of water of crystallisation much more easily than the seventh, which requires a temperature of 200°. Again, the naturally occurring monohydrated salt, kieserite, requires prolonged boiling with water before it will dissolve. There appears, then, every good reason for supposing that one of the seven molecules of water is water of constitution, and is presumably bound to the acidic portion of the molecule, with the result that one of the doubly co-ordinated oxygen atoms is developed and forms two hydroxyl groups; the constitution may therefore be written $[SO_3\cdot 2OH]Mg,6H_2O$. Now there are three possible spacial formulæ for the co-ordinated portion of the molecule:

FIG. 3.



In the first two formulæ the hydroxyl groups occupy *cis*-positions, but in the third formula, *trans*-positions. The first formula possesses two planes of symmetry, the second, a single plane of symmetry; so neither is of an enantiomorphous character. The third *trans*-formula, although possessing a trigonal axis of symmetry, has neither plane, centre, nor axis of alternating symmetry, and is consequently non-superposable with its mirror image. It is accordingly suggested that the *trans*-formula represents the stereochemical constitution of the acidic radicle of magnesium sulphate, and confers enantiomorphism on the molecule as a whole. Since in solution the magnesium is separately ionisable, it lies of necessity outside the co-ordination sphere of the sulphur, and it appears reasonable to suppose that it is in turn co-ordinatively surrounded by the six molecules of water of crystallisation.

*Sodium Dihydrogen Phosphate*, $NaH_2PO_4,H_2O$.—The constitution of this compound would appear to be analogous to that of the foregoing, namely, $[PO_3{\cdot}2OH]NaH_2$, in which, as before, the hydroxyl groups occupy the *trans*-position.

*Schlippe's Salt*, $Na_3SbS_4,9H_2O$.—No data exist concerning a possible division of the water into water of constitution and of crystallisation. Enantiomorphous formulæ are, indeed, obtainable by taking one, two, three, or four molecules as water of constitution, each molecule forming with a corresponding double bond sulphur atom the groups SH and OH. The number of possible spacial formulæ are respectively: one active and one inactive, four active and four inactive, two active and two inactive, one active and four inactive. In view of this, it is impossible to indicate any particular formula for this salt.

*Sodium Uranyl Acetate*, $NaUO_2(C_2H_3O_2)_3$.—If, as seems likely, the sodium atom be supposed to lie outside the co-ordination sphere of the uranium, the co-ordination number of the latter becomes seven, and it becomes impossible to indicate, a priori, any likely configuration. If, on the other hand, the unlikely assumption be made that the sodium makes up the eighth co-ordination number, the number of possible spacial formulæ can be easily worked out and proves to be four—three active and one inactive.

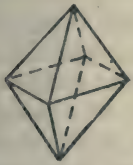
### *Collateral Evidence in Favour of the Constitutions Suggested.*

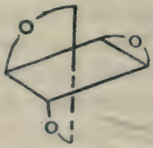
The constitutions which have been suggested for the first two compounds discussed are based fundamentally on the assumption that a certain amount of water of constitution is included in the acidic part of the molecule, and confers on it enantiomorphism. Now there are, as a matter of fact, two possible spacial formulæ for the anhydrous group ($SO_4$), both of which possess planes of symmetry; with neither of these possible configurations, then, would optical activity be expected. This expectation is fully in accordance with the facts, for there is only one case known of optical activity amongst the large class of anhydrous sulphates, orthophosphates, orthosilicates, periodates, perruthenates, etc., namely, potassium lithium sulphate, $KLiSO_4$. This substance crystallises in the hexagonal system in a class which admits of the presence of hexagonal screw axes, and accordingly even in this case no enantiomorphism of molecular configuration is called for.

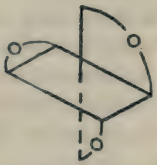
The lowering of the symmetry of the molecular configuration by the presence of a molecule of water of crystallisation is of quite frequent occurrence, as is evidenced by the appearance of monohydrated salts in enantiomorphous forms. Thus, the monohydrated lithium sulphate, $Li_2SO_4,H_2O$, is one of the classical examples of enantiomorphism in the monoclinic system. The proof of the presence of optical activity in such a crystal is a somewhat laborious process, since the rotatory power can only be observed in two sections, which have to be ground with great accuracy. It is proposed to undertake this work when the necessary grinding instrument has been obtained.

### *Constitution of Substances with Co-ordination Number Six.*

The two substances to be considered are sodium chlorate and its analogue sodium bromate, which must naturally have a similar constitution. Since the co-ordination number is six, the co-ordination figure is a regular octahedron, at the centre of which is situated the chlorine atom, with its six co-ordination valencies directed towards the six corners. When the six valencies are satisfied by three doubly bound oxygen atoms, the group $ClO_3$ becomes enantiomorphous:







The above constitution is analogous to the one suggested by Werner for the complex chromium oxalate group in the optically active potassium chromium oxalate.

### *Constitution of the Substances in the State of Solution.*

The question must now be considered whether the substances under discussion retain the same constitution when dissolved or liquefied, or whether a radical change takes place so as to yield a molecule with a different formula. There appears to be only one available source of evidence in this connexion, namely, ionisation phenomena, which, in fact, point to the conclusion that there is no change of constitution when the substances are dissolved. Sodium chlorate, for example, undergoes electrolytic dissociation into $ClO_3$ and Na ions, that is, into the co-ordinated and the unco-ordinated parts of the molecules. Again, a solution of magnesium sulphate contains Mg and $SO_4$ ions, and since the prevailing tendency of opinion is to assume that each ion is surrounded by an envelope of several water molecules, the single water molecule which was received into the co-ordination sphere may perhaps be looked upon as constituting one of the relatively large number which surround the $SO_4$ ion in solution.

If the constitution remains unaltered during the passage of the substance into solution, some explanation must be forthcoming of the inactivity of the solution. This inactivity is probably due to autoracemisation. That there is nothing inherently improbable in this view will perhaps be generally admitted if the constitution of the compounds be compared with those of the substances which have been successfully resolved by Werner. The latter are very prone to racemisation, although the bivalent groups attached to the central atom are of a complex character; representative examples of such groups are ethylenediamine, dipyridyl, and $C_2O_4$. In particular, the optically active antipodes of potassium chromic oxalate, $K_3Cr(C_2O_4)_3,H_2O$, are completely racemised in aqueous solution in seventy-five minutes (Werner, *Ber.*, 1912, **45**, 3063). Now racemisation in such a molecule involves either a flyping of the molecule or a loosening of one of the attachments of each of two $(C_2O_4)$ groups, a rotation of each group about the free ends through an angle of 60°, and a subsequent coupling up. If this process is so easy with a group like $C_2O_4$, how much more readily should it occur with doubly bound oxygen atoms, especially as it could be brought about by alternate hydroxylation and dehydration. It is conceivable that autoracemisation should be practically instantaneous on dissolving the crystal. Since no previous experiments appear to have been carried out on this subject, it is proposed to investigate the point, although a positive result is perhaps not to be hoped for.

The reverse change, that is, the crystallisation of the inactive supersaturated solution so as to yield either one or the other crystalline antipode, is equally feasible. When the substance crystallises, the solid phase may be either a conglomerate of active crystals or a racemate. In the former case the accidental appearance of a surplus of *d*- over *l*-crystals will be automatically accompanied by a racemisation of *l*- into *d*-molecules in solution, so that the solution remains inactive.

### *The Relationship of Sodium Chlorate and Sodium Nitrate.*

The crystalline forms of these two substances are not isomorphous at the ordinary temperature, but at higher temperatures sodium chlorate crystallises in a second modification, isomorphous with the well-known rhombohedral form of sodium nitrate. It must therefore be concluded that the two substances have a similar constitution, and the question must now be entertained why sodium nitrate is not optically active. The absence of rotatory power in crystals of sodium nitrate receives a satisfactory explanation if it be assumed to be a racemate, that is, a molecular compound of the two antipodes, which in the free state would be isomorphous with sodium chlorate. Some confirmation of the correctness of this view is derived from the following interesting consideration: If a *d*- and an *l*-molecule of sodium nitrate, having configurations similar to those given for sodium chlorate, be allowed to interpenetrate in the most symmetrical way possible, then the symmetry of the racemic molecule thus obtained is found to be identical in every respect with that of a crystal of sodium nitrate, and, moreover, is in complete harmony with the rhombohedral form.

Again, the dimorphism of sodium chlorate now acquires a new significance. The rhombohedral modification of this salt, being isomorphous with the racemic nitrate, must itself also be a racemic compound; and the "dimorphism" of sodium chlorate becomes precisely analogous to that of sodium ammonium tartrate, that is, there is a transition temperature above and below which the racemate and the conglomerate of optical antipodes are the stable phases respectively. The crystalline form, composition, and physical properties of mixed crystals of sodium chlorate and nitrate are also in full accord with the present interpretation. Mallard (*Bull. Soc. franç. Min.*, 1884, **7**, 352) has found that at the ordinary temperature the rhombohedral sodium nitrate will take up as much as 22·5 per cent. of sodium chlorate; the optically active, cubic sodium chlorate, however, does not appreciably dissolve the nitrate.

In conclusion, we wish to express our grateful thanks to Prof. H. Hilton for much valuable advice on the theory of crystal structure.

CHEMICAL AND MINERALOGICAL DEPARTMENTS,
UNIVERSITY MUSEUM, OXFORD.

# LXXXVI.—*The Preparation of Pure Bromine.*

By ALEXANDER SCOTT.

EVERYONE interested in atomic weight work realises the fundamental importance of the reaction between silver and bromides on which so much of the work of Stas and others depends. Any improvement in the preparation either of pure silver or pure bromine therefore requires no apology.

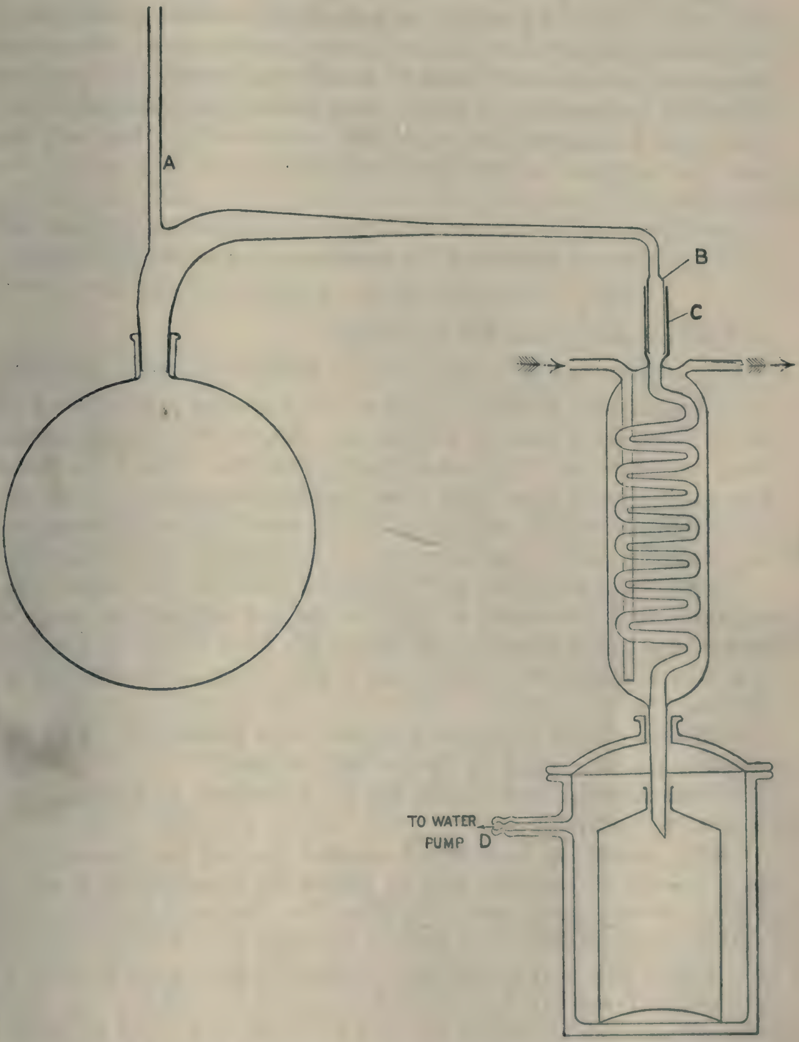
The method for the preparation of pure bromine described by Stas in 1876 (*Mem. Acad. Sci. Bruxelles*, 1881, **42**, 90) cannot be regarded as altogether satisfactory. He distils his bromine from a strong solution of potassium bromide containing in suspension zinc oxide prepared by ignition of the nitrate. This, he says, removes any iodine as iodate, and, of course, any chlorine decomposes an equivalent amount of potassium bromide. Now, however carefully the zinc oxide is prepared in this way, it is almost certain to contain sufficient nitrogen oxides to contaminate the bromine with traces at least of nitric acid. Further, all the organic chlorides and bromides which were originally in the bromine are left in the product so purified. For the great majority of purposes they fortunately do not much matter.

Having to prepare a large quantity of bromine which must be free from organic compounds as well as the other halogens, it occurred to me to prepare it from potassium bromide which had been completely freed from iodine either as iodide or iodate. This was done by boiling a solution of 1500 grams of the bromide in an equal weight of water first with a few crystals of potassium metabisulphite and about 5 c.c. of concentrated sulphuric acid, then adding 100 c.c. of saturated bromine water, distilling off the excess of bromine, adding another 100 c.c. of bromine water, distilling off once more, and, after neutralisation with potassium carbonate, evaporating to dryness. The dried bromide was now fused with potassium dichromate (which had previously been fused) in the proportion of 500 grams of bromide to 200 grams of dichromate. This leaves an excess of bromide sufficient to retain any quantity of chlorine likely to be present. 1050 Grams of the fused mass broken up into pieces the size of hazel nuts were now treated with a *cold* mixture of 450 c.c. of concentrated sulphuric acid with 700 c.c. of water. Any organic matter in this mixture was destroyed by adding a small quantity of potassium permanganate. The above quantities give about 470 grams of bromine, and on the addition of an excess of dichromate a further 30 grams of bromine are obtained, which ought to contain all the chlorine.

Altogether, I prepared about 3250 grams of the pure bromine, together with an additional 183 grams possibly containing chlorine. The purity of the bromine was indicated clearly by the fact that these 183 grams only contained 4 to 5 *milligrams* of chlorine. The 3250 grams were, however, dissolved in potassium bromide solution (which had been freed from iodine as above described), and distilled from it so that I believe I have now got bromine pure enough for my work.

The apparatus employed for the distillations above described is very simple, and the diagram practically explains itself. The chief points to be attended to are that the tube *A* should be about

150 mm. long, and of just sufficient diameter to take a thermometer which can be replaced by a tube for bubbling air through the liquid or simply by a glass rod. The first drops of liquid seal in the air between the lower end of *A* and the small piece of india-rubber tubing which keeps the thermometer, etc., in position. The tube *B* also should just fit loosely into the condenser tube *C*, and in distilling bromine a drop of water is a sufficient seal between *B* and the condenser. The bottle acting as a receiver is placed in a



Witt's filtering apparatus with the funnel removed, and *D* connected with a water-pump drawing in a gentle current of air. By means of this apparatus any quantity of bromine may be distilled without its odour causing the slightest inconvenience.

In endeavouring to determine the quantity of iodine which could be detected, and, if possible, its amount determined, I was led to try the effect of sodium hydroxide instead of zinc oxide as a means of removing it from the bromine. Bromates of the alkali metals are so readily decomposed by iodine, even without the addition of any acid, that I thought this might act satisfactorily. Not only so, but the bromide formed simultaneously should also retain the chlorine.

The result of the experiment was successful far beyond my anticipations, and instead of the reaction, which is usually written:

$$3Br_2 + 6NaOH = 5NaBr + NaBrO_3 + 3H_2O,$$

we have something like the following:

$$2Cl_2 + 3Br_2 + I_2 + 12NaOH = 4NaCl + 6NaBr + 2NaIO_3 + 6H_2O.$$

To begin with, I added to 10 c.c. of bromine 3 milligrams of iodine (that is, 1 part in 10,000) and then 4 or 5 c.c. of water, along with 1 c.c. of *N*-sodium hydroxide solution. This was shaken vigorously several times, and then the bromine separated from the aqueous liquid, which was heated on the water-bath until colourless, then treated with a slight excess of sulphurous acid; after this excess had been boiled off and the liquid cooled, it was tested with sulphuric acid containing a little nitrite and chloroform, when a very strong iodine reaction was obtained. With 10 c.c. of bromine it is easy to detect the presence of 1 part of iodine in 100,000 of bromine.

Similarly, a known weight of chlorine was passed into 10 c.c. of bromine, and was found to be similarly removed.

Neither chlorine nor iodine could be detected in the residual bromine respectively.

I hope shortly to describe in detail a method for determining the amounts of chlorine and of iodine in bromine, even when present in very small quantity, but as at present employed it is capable of simplification in one or two respects. I shall content myself with practical proofs that bromine shaken up once with a sufficiency of sodium hydroxide solution to combine with the chlorine and iodine present, is to all intents and purposes freed completely from these elements. No doubt for atomic-weight work it would be safer to treat commercial bromine, say, three times, distilling it from a small quantity of very dilute soda finally.

A few examples taken from my notebook will indicate the quality of the bromine thus produced. The equivalents found with the solutions employed are all rather high. This is due to a small quantity of the halogen being driven off during fusion, and consequently the presence of a small quantity of hydroxide or carbonate, which, of course, raises the equivalent.

The purest bromine prepared as above described was shaken with 5 c.c. of *N*-sodium hydroxide, the aqueous solution evaporated to dryness, and the residue fused so as to decompose the bromate. This residue weighed 0·4737 gram, requiring 45·7 c.c. of *N*/10-silver nitrate:

$$\text{Equivalent} = 103{\cdot}65\,;$$

between 0·120 and 0·130 gram of chlorine was passed into 5 c.c. of bromine, and then the bromine shaken with 10 c.c. of *N*-sodium hydroxide, and treated as above, when the residue, weighing 0·8345 gram, required 94·45 c.c.:

$$\text{Equivalent} = 88{\cdot}35,$$

and chlorine = 0·1232 gram.

The bromine remaining was now shaken with 5 c.c. of *N*-sodium hydroxide as above, when the residue weighed 0·5103 gram, requiring 49·15 c.c. of *N*/10-silver nitrate:

$$\text{Equivalent} = 103{\cdot}8.$$

The residual bromine was again treated with 5 c.c. of *N*-sodium hydroxide and treated as above, when the residue weighed 0·5023 gram, requiring 48·45 c.c., whence the

$$\text{Equivalent} = 103{\cdot}7.$$

The 183 grams of bromine referred to previously as possibly containing chlorine (p. 848) were similarly treated with 5 c.c. of *N*-sodium hydroxide, when the residue weighed 0·4899 gram and required 47·7 c.c. of *N*/10-silver nitrate, giving an equivalent = 102·7, corresponding with 0·0044 gram of chlorine.

The bromine remaining was again treated, when the residue weighing 0·4991 gram required 48·15 c.c., and gave the equivalent = 103·65.

These examples seem to prove conclusively that bromine treated with sodium hydroxide even in such small quantities as above indicated is completely freed from both chlorine and iodine.

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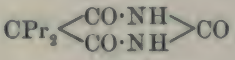
# LXXXVII.—*The Application of Hofmann's Reaction to Dialkylacetamides.*

By Frank Lee Pyman.

In the course of work on the relation between chemical constitution and physiological action in hypnotic substances, it was thought desirable to prepare α-propylbutyryl-δ-heptylcarbamide (I) for the following reasons. It is known that α-propylbutyrylcarbamide (II) has hypnotic properties, and so also have various monoalkylcarbamides. α-Propylbutyryl-δ-heptylcarbamide might therefore be expected to have the combined hypnotic properties of the two classes of compounds; further, it would be somewhat similarly constituted to dipropylbarbituric acid ("proponal") (III), which is a powerful hypnotic:

$CHPr_2 \cdot CO \cdot NH \cdot CO \cdot NH \cdot CHPr_2$ (I.) $CHPr_2 \cdot CO \cdot NH \cdot CO \cdot NH_2$ (II.)



$$CPr_2 \begin{matrix} \diagup CO \cdot NH \diagdown \\ \diagdown CO \cdot NH \diagup \end{matrix} CO$$

(III.)

The obvious method indicated in the literature for the preparation of α-propylbutyryl-δ-heptylcarbamide was Hofmann's reaction, namely, to treat two molecular proportions of α-propylvaleramide, $CHPr_2 \cdot CO \cdot NH_2$, with one molecular proportion of bromine and aqueous potassium hydroxide. Experiments showed, however, that this method did not give the desired result, for in the place of the expected compound a mixture of *s-di-δ-heptylcarbamide*, $(CHPr_2 \cdot NH)_2CO$, and unchanged α-propylvaleramide was obtained. This is entirely at variance with the behaviour of the normal aliphatic acid amides in similar circumstances, and gave rise to the investigation herein recorded.

It is now shown that the dialkylacetamides—in particular α-propylvaleramide, with which the work has chiefly been carried out—do not behave precisely similarly to the normal aliphatic acid amides in respect of their behaviour to bromine and alkali. The differences in behaviour between the acid amides of the two classes may be compared under three headings, namely, (1) formation of the bromoamide, (2) formation of the lower amine, and (3) formation of the acylalkylcarbamide.

## (1) *Formation of the Bromoamide.*

Hofmann (*Ber.*, 1882, **15**, 407, 752) has shown that when a normal aliphatic acid amide is treated with bromine (1 molecule) and sodium or potassium hydroxide (1 molecule), the bromoamide is produced as follows:

$$R{\cdot}CO{\cdot}NH_2 + Br_2 + KOH = R{\cdot}CO{\cdot}NHBr + KBr + H_2O.$$

The bromoamides of acetic and propionic acids were isolated as pure, crystalline compounds, but neither *n*-butyrobromoamide nor any of the higher bromoamides could be isolated in a crystalline condition; *iso*butyramide, however, readily gave a crystalline bromoamide. It has now been found that *α-ethylbutyrobromoamide* and *α-propylvalerobromoamide* can also readily be isolated in crystalline form in almost quantitative yield.

### (2) *Formation of the Lower Amine.*

Hofmann (*Ber.*, 1882, **15**, 762; 1884, **17**, 1406, 1920) has shown that the preparation of amines from the normal aliphatic acid amides (1 mol.) by the action of bromine (1 mol.) and excess of aqueous potassium hydroxide:

$$R{\cdot}CO{\cdot}NH_2 + Br_2 + 4KOH = R{\cdot}NH_2 + 2KBr + K_2CO_3 + 2H_2O,$$

does not proceed smoothly above the fifth member of the series, and that this is due partly to the formation of nitriles:

$$R{\cdot}CH_2{\cdot}CO{\cdot}NH_2 \longrightarrow R{\cdot}CH_2{\cdot}NH_2 \longrightarrow R{\cdot}CH_2{\cdot}NBr_2 \longrightarrow R{\cdot}CN,$$

and partly to the formation of the corresponding acylalkylcarbamide.

Thus, *n*-octoamide (which is isomeric with α-propylvaleramide) gives only a 30 per cent. yield of *n*-heptylamine.

α-Propylvalerobromoamide, however, when treated with an excess of aqueous sodium hydroxide, readily gives an 84 per cent. yield of δ-aminoheptane, $CHPr_2{\cdot}NH_2$; in this case, of course, no nitrile formation is possible, and as will be shown later there is very little tendency to the formation of the acylalkylcarbamide.

### (3) *Formation of the Acylalkylcarbamide.*

Hofmann (*Ber.*, 1882, **15**, 762) has shown that when the normal aliphatic acid amides (2 mols.) are treated with bromine (1 mol.) and aqueous potassium hydroxide, acylalkylcarbamides are produced in excellent yields throughout the series up to stearamide, the highest member tested:

$$2R{\cdot}CO{\cdot}NH_2 + Br_2 + 2KOH = R{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}R + 2KBr + 2H_2O,$$

and states, for instance, that the yield of heptohexylcarbamide from heptoamide, $C_6H_{13}{\cdot}CO{\cdot}NH_2$, is nearly quantitative, and that the reaction proceeds with increasing readiness from the eighth member of the series onwards. *n*-Octoamide (the isomeride of α-propylvaleramide) would, therefore, give an excellent yield of the corresponding acylalkylcarbamide. He tested also three aliphatic acid amides outside the normal series, namely, *iso*butyramide, $CHMe_2\cdot CO\cdot NH_2$, *iso*valeramide, $CHMe_2\cdot CH_2\cdot CO\cdot NH_2$, and *iso*hexoamide, $CHMe_2\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$; the two latter gave normal results, for the corresponding acylalkylcarbamides were obtained, and there is no mention of any by-products. In the case of *iso*butyramide, however, the action of bromine (1 mol.) and aqueous potassium hydroxide on 2 molecules of the acid amide gave rise to a mixture of the acylalkylcarbamide, namely, *iso*butyro*iso*propylcarbamide, with a small proportion of *s*-di-*iso*propylcarbamide:

$$CHMe_2\cdot CO\cdot NH_2 \longrightarrow CHMe_2\cdot CO\cdot NH\cdot CO\cdot NH\cdot CHMe_2 \text{ and } CHMe_2\cdot NH\cdot CO\cdot NH\cdot CHMe_2.$$

In the long series of acylalkylcarbamides prepared from aliphatic acid amides by Hofmann and subsequent investigators this is the only case in which a by-product of this type has hitherto been observed.

*iso*Butyramide is, of course, the simplest possible dialkylacetamide. Now it has already been stated that the action of bromine (1 mol.) and alkali on α-propylvaleramide (2 mols.) gave a mixture of *s*-di-δ-heptylcarbamide and α-propylvaleramide instead of the acylalkylcarbamide, and it has further been found that α-methylbutyramide, $CHMeEt\cdot CO\cdot NH_2$, α-ethylbutyramide, $CHEt_2\cdot CO\cdot NH_2$, and α-ethylvaleramide, $CHEtPr\cdot CO\cdot NH_2$, when similarly treated also yield mixtures containing the corresponding *s*-dialkylcarbamides and the unchanged acetamides.

In order to inquire into the cause of the divergence in the behaviour between the normal aliphatic acid amides and the dialkylacetamides, the following experiments were carried out with derivatives of α-propylvaleramide.

In the first place, α-propylvalerobromoamide was prepared. This substance appears to have been obtained previously by Fuchs (*Zeitsch. angew. Chem.*, 1904, **17**, 1505) for the purpose of a physiological examination, but its chemical and physical properties have not hitherto been described. It was readily obtained in the usual way following the procedure described by Mauguin (*Ann. Chim. Phys.*, 1911, [viii], **22**, 297). *α-Ethylbutyrobromoamide* was also prepared in a similar manner. The preparation of α-propylbutyryl-δ-heptylcarbamide was then attempted with the pure isolated α-propylvalerobromoamide in the place of the solution of α-propylvaleramide in bromine. α-Propylvalerobromoamide (1 mol.) was mixed with α-propylvaleramide (1 mol.) and warmed with aqueous sodium hydroxide (1 mol.), when again a mixture of *s*-di-δ-heptylcarbamide with unchanged α-propylvaleramide was obtained.

In order to determine whether the failure to combine was due to the inertness of the α-propylvaleramide, a similar experiment was carried out, using acetamide in its place, but here again a mixture containing *s*-di-δ-heptylcarbamide was obtained. It was thus shown that the nature of the acid amide was not the cause of the failure to form the desired compound. The action of aqueous sodium hydroxide (1 mol.) on α-propylvalerobromoamide (1 mol.) was then examined; the product when distilled in a current of steam gave *δ-carbimidoheptane* in a yield amounting to 80 per cent.

$$\mathrm{CHPr_2{\cdot}CO{\cdot}NHBr + NaOH = CHPr_2{\cdot}N{:}CO + NaBr + H_2O}$$

of the theoretical, and a mixture of *s*-di-δ-heptylcarbamide and α-propylbutyryl-δ-heptylcarbamide remained in the residual liquor.

*δ-Carbimidoheptane* is only slowly altered by boiling water, for it remained largely unchanged after boiling for one and a-half hours with five times its weight of water. Boiling aqueous sodium hydroxide gradually converts it almost quantitatively into *s*-di-δ-heptylcarbamide:

$$\mathrm{2CHPr_2{\cdot}N{:}CO + 2NaOH = (CHPr_2{\cdot}NH)_2CO + Na_2CO_3,}$$

and with cold aqueous ammonia it yields *δ-heptylcarbamide*:

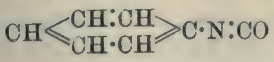
$$\mathrm{CHPr_2{\cdot}N{:}CO + NH_3 = CHPr_2{\cdot}NH{\cdot}CO{\cdot}NH_2.}$$

It follows from the experiments previously described that δ-carbimidoheptane, even in a nascent condition, does not combine—or at most combines to a very slight extent—with acid amides in the presence of water, but it was found that the required *α-propylbutyryl-δ-heptylcarbamide* could be prepared by directly heating together δ-carbimidoheptane and α-propylvaleramide:

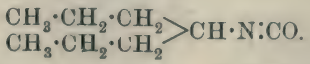
$$\mathrm{CHPr_2{\cdot}N{:}CO + CHPr_2{\cdot}CO{\cdot}NH_2 = CHPr_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CHPr_2.}$$

It thus appears that the behaviour of δ-carbimidoheptane resembles more closely that of phenylcarbimide than that of the normal aliphatic carbimides, although it is less readily affected by water than phenylcarbimide, which is quickly changed into *s*-diphenylcarbamide; thus Kühn (*Ber.*, 1884, **17**, 2880) found that phenylcarbimide when heated with acid amides gave acylphenylcarbamides only in the absence of water, and that in the presence of water diphenylcarbamide was formed.

This similarity of behaviour and divergence from that of the normal aliphatic acid amides may possibly be accounted for by the similarity of steric structure of the two compounds.



$$\mathrm{CH}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{\cdot}CH}\end{matrix}>\mathrm{C{\cdot}N{:}CO}$$



$$\begin{matrix}\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2}\\ \mathrm{CH_3{\cdot}CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CH{\cdot}N{:}CO.}$$

In connexion with α-propylvalerobromoamide, the following point may be mentioned. Jeffreys (*Amer. Chem. J.*, 1899, **22**, 14) has shown that normal aliphatic bromoamides react with sodium methoxide, and less readily with sodium ethoxide, to yield esters of the corresponding alkylcarbamates. α-Propylvalerobromoamide behaves similarly in this respect, giving excellent yields of methyl and ethyl δ-heptylcarbamates in the two cases:

$$CHPr_2{\cdot}CO{\cdot}NHBr + NaOMe = CHPr_2{\cdot}NH{\cdot}CO_2Me + NaBr.$$

The results of the physiological examination of α-propylbutyryl-δ-heptylcarbamide and methyl δ-heptylcarbamate were disappointing, neither compound having any marked hypnotic action.

## EXPERIMENTAL.

### *Action of Sodium Hydroxide on α-Propylvaleramide* (2 *mols.*) *and Bromine* (1 *mol.*).

7·1 Grams of α-propylvaleramide were mixed with 4 grams of bromine, and 20 c.c. of 10 per cent. aqueous sodium hydroxide were added, the mixture being cooled in water. After heating on the water-bath, the oil floating on the surface of the aqueous layer became reddish-brown. A further quantity of 10 c.c. of 10 per cent. aqueous sodium hydroxide was then added, and the mixture heated for another half-an-hour, when the oil became almost colourless. The mixture was then cooled, and the solidified oil collected and washed with water, when it amounted to 5·9 grams, melting at 88—90°. On crystallisation from alcohol, 1·5 grams of crude *s*-di-δ-heptylcarbamide melting at 190—200° first separated, and by recrystallisation of this from the same solvent 1·2 grams of the pure compound were obtained. The mother liquors deposited on dilution with water 3·5 grams of crude α-propylvaleramide, which melted at 117°, the mixture with the pure amide (m. p. 124°) melting at 119°. The ultimate mother liquors when evaporated to dryness left a solid, which after draining on porous porcelain melted at 95—105°.

It is thus clear that very little, if any, α-propylbutyryl-δ-heptylcarbamide, which, it is subsequently shown, melts at 89—90°, can have been formed in this reaction.

In a larger experiment carried out with 35 grams of α-propylvaleramide, 10 grams of the pure *s*-di-δ-heptylcarbamide were obtained.

s-*Di-δ-heptylcarbamide*, $(CHPr_2{\cdot}NH)CO$, crystallises from alcohol in colourless needles, which melt at 239—241° (corr.). It is insoluble in boiling water, dilute acid, or alkalis, sparingly soluble in cold alcohol or ether, but readily so in hot alcohol:

0·1192 gave 0·3060 $CO_2$ and 0·1341 $H_2O$. C = 70·0; H = 12·6.
0·1354 „ 12·9 c.c. $N_2$ at 20° and 760 mm. N = 11·2.
$C_{15}H_{32}ON_2$ requires C = 70·3; H = 12·6; N = 10·9 per cent.

It dissolves in concentrated sulphuric acid, and is reprecipitated on dilution with water. It is not decomposed by boiling 50 per cent. aqueous potassium hydroxide, but when it is distilled from a metal-bath with fused potassium hydroxide containing a few drops of water, δ-aminoheptane passes over between 240° and 320°, accompanied by some unchanged carbamide, and is obtained in a yield amounting to 71 per cent. of the theoretical, allowing for the unchanged material.

The preparation and properties of the following carbamides are similar to the above except that the yields diminish with the size of the molecule.

s-*Di-γ-hexylcarbamide*, $(CHEtPr{\cdot}NH)_2CO$, which melts at 220—222° (corr.):

0·1500 gave 0·3760 $CO_2$ and 0·1647 $H_2O$. C = 68·4; H = 12·3.
$C_{13}H_{28}ON_2$ requires C = 68·4; H = 12·4 per cent.

s-*Di-γ-amylcarbamide*, $(CHEt_2{\cdot}NH)_2CO$, which melts at 212—214° (corr.):

0·1200 gave 14·6 c.c. $N_2$ at 23° and 770 mm. N = 14·3.
$C_{11}H_{24}ON_2$ requires N = 14·0 per cent.

*s*-Di-β-butylcarbamide, $(CHMeEt{\cdot}NH)_2CO$, which melted at 134—135° (corr.). (Found, C = 63·1; H = 11·4; N = 16·0. Calc., C = 62·8; H = 11·6; N = 16·3 per cent.) This substance has previously been described by A. E. Dixon (T., 1895, **67**, 651), who gives its melting point as 137—138°.

### *α-Propylvalerobromoamide*, $CHPr_2{\cdot}CO{\cdot}NHBr$.

This substance was prepared by a method similar to that employed by Mauguin (*Ann. Chim. Phys.*, 1911, [viii], **22**, 297) for the preparation of *iso*butyrobromoamide.

11·4 Grams of α-propylvaleramide were dissolved in 40 c.c. of chloroform, and 12·8 grams of bromine added. The solution was then cooled to −10°, and a solution of 4·5 grams of potassium hydroxide in 160 c.c. of water added gradually with thorough stirring, keeping the temperature below 0°. The product, consisting mainly of ice, was then warmed to 5°, and the separated solid collected, washed with a little water, and drained on porous porcelain. It represented nearly pure bromoamide, amounting usually to from 14 to 15 grams, that is, 79 to 84 per cent. of the theoretical, and melted at 109° or a degree or so higher. For analysis it was recrystallised from dry ether, when the pure bromoamide then separated in colourless, prismatic needles, which melted at 116° (corr.) to a red liquid:

0·1328 gave 0·2108 $CO_2$ and 0·0888 $H_2O$. C=43·3; H=7·5.
0·1658 „ 0·1390 AgBr. Br=35·7.
$C_8H_{16}ONBr$ requires C=43·2; H=7·3; Br=36·0 per cent.

*a-Propylvalerobromoamide* is insoluble in cold water, readily soluble in alcohol, moderately so in warm, but sparingly so in cold, ether. It decomposes and turns yellow after keeping for a few days.

In the experiments described below, the crude α-propylvalerobromoamide melting at 109° or a little higher was employed.

### *a-Ethylbutyrobromoamide*, $CHEt_2·CO·NHBr$.

This substance was prepared in the same way as α-propylvalerobromoamide, except that it did not crystallise from the product but remained dissolved in the chloroform. After separating this solvent from the aqueous solution and allowing it to evaporate spontaneously, α-ethylbutyrobromoamide remained. It was purified by crystallisation from dry ether, from which it separates in flat, colourless needles, melting at 86—87° (corr.). It is insoluble in water, readily soluble in alcohol, moderately so in warm, but sparingly so in cold ether:

0·1410 gave 0·1920 $CO_2$ and 0·0752 $H_2O$. C=37·1; H=6·0.
0·1570 „ 0·1532 AgBr. Br=41·2.
$C_6H_{12}ONBr$ requires C=37·1; H=6·2; Br=41·2 per cent.

It gives an excellent yield of γ-aminopentane when distilled with an excess of 10 per cent. aqueous sodium hydroxide.

### *a-Propylvalerobromoamide* (1 *mol.*), *a-Propylvaleramide* (1 *mol.*), *and Sodium Hydroxide* (1 *mol.*).

2·2 Grams of α-propylvalerobromoamide, 1·4 grams of α-propylvaleramide, and 4 c.c. of 10 per cent. aqueous sodium hydroxide were shaken together when the mixture became warm. It was heated for an hour on the water-bath and then cooled. The separated solid was collected and washed with water, when it amounted to 2·6 grams melting at about 88—90°. After fractional crystallisation from alcohol, 0·75 gram of *s*-di-δ-heptylcarbamide (m. p. 235°) and 1·1 grams of α-propylvaleramide (m. p. 122°) were isolated from the mixture.

Little, if any, combination between the δ-carbimidoheptane, which would be formed by the action of the alkali on the bromoamide, and the α-propylvaleramide can therefore have taken place.

A similar result was arrived at in the case of α-ethylbutyrobromoamide and α-ethylbutyramide.

### *α-Propylvalerobromoamide* (1 *mol.*), *Acetamide* (1 *mol.*), *and Sodium Hydroxide* (1 *mol.*).

2·2 Grams of α-propylvalerobromoamide, 0·6 gram of acetamide, and 4 c.c. of 10 per cent. aqueous sodium hydroxide were mixed, digested for one hour on the water-bath, and distilled in a current of steam. Only traces of oil passed over with the steam, and the residue, which was obviously a mixture, readily gave on crystallisation from alcohol a quantity of *s*-diheptylcarbamide. After 0·3 gram of this compound had been isolated in a pure state the separation was not carried out further.

### *α-Propylvalerobromoamide and Excess of Sodium Hydroxide. Formation of δ-Aminoheptane.*

11·1 Grams of α-propylvalerobromoamide were shaken with 111 c.c. of 10 per cent. aqueous sodium hydroxide. After keeping for ten minutes the solution was distilled in a current of steam, when the amine passed over as an oil, which was sparingly soluble in water. The distillation was continued so long as an alkaline distillate was obtained. The latter was then slightly acidified with hydrochloric acid and evaporated to dryness, when 6·4 grams of δ-aminoheptane hydrochloride melting at 240° were obtained, that is, 84 per cent. of the theoretical. After crystallisation from water this salt formed needles, which melted at 246—247° (corr.). It is readily soluble in cold water, and very readily so in hot water or absolute alcohol. (Found, C = 54·9; H = 11·7; Cl = 23·3. Calc., C = 55·4; H = 11·3; Cl = 23·4 per cent.) Noyes (*Amer. Chem. J.*, 1893, **15**, 542), who has previously prepared δ-aminoheptane by the reduction of dipropylketoxime, gives the melting point of this salt as 241—242°.

*δ-Aminoheptane platinichloride* crystallises from water in plates, which decompose at about 235° (corr.). It is readily soluble in hot, but rather sparingly so in cold water:

0·3158 (dried at 100°) gave 0·0955 Pt. Pt = 30·2.

$(C_7H_{17}N)_2,H_2PtCl_6$ requires Pt = 30·4 per cent.

### *α-Propylvalerobromoamide* (1 *mol.*) *and Sodium Hydroxide* (1 *mol.*). *Formation of δ-Carbimidoheptane*, $CHPr_2\cdot N\colon CO$.

11·1 Grams of α-propylvalerobromoamide were shaken with a solution of 2 grams of sodium hydroxide in 20 c.c. of water. The mixture became warm, and the solid was converted into an oil.

On distillation in a current of steam the product was separated into two fractions.

δ-*Carbimidoheptane* passed over with the steam, and after separation from the water amounted to 5·6 grams, that is, 80 per cent. of the theoretical yield. After distillation under normal pressure it passed over almost completely at 171° (corr.) as a colourless oil:

0·1590 gave 0·3958 $CO_2$ and 0·1564 $H_2O$. $C=67·9$; $H=11·0$.

$C_8H_{15}ON$ requires $C=68·1$; $H=10·7$ per cent.

The residual liquor after the steam distillation contained an oil which solidified on cooling. This amounted to 1·5 grams, and melted at about 95—100° after sintering earlier. Treatment with ether separated it into *s*-di-δ-heptylcarbamide, which is sparingly soluble in this solvent, and α-propylbutyryl-δ-heptylcarbamide, which is readily soluble.

*Action of Boiling Water and Sodium Hydroxide on* δ-*Carbimidoheptane.*—Two grams of δ-carbimidoheptane were boiled with 10 c.c. of water for one and a-half hours under a reflux condenser; on cooling, the oil remained largely unchanged, still having the characteristic odour and power of irritating the eyes possessed by carbimides; it contained, however, a small amount of silky needles, probably *s*-di-δ-heptylcarbamide. Five c.c. of water containing 1·5 grams of sodium hydroxide were then added, and the mixture again boiled for one and a-half hours. The resulting solid was then collected, washed with water, and dried at 100°, when 1·6 grams of pure *s*-di-δ-heptylcarbamide melting at 237° were obtained; that is, 89 per cent. of the theoretical.

*Action of Ammonia on* δ-*Carbimidoheptane.*—When δ-carbimidoheptane is shaken with 10 per cent. aqueous ammonia it is gradually converted into δ-*heptylcarbamide*, $CHPr_2{\cdot}NH{\cdot}CO{\cdot}NH_2$, which crystallises from alcohol in colourless needles, melting at 173° (corr.):

0·0820 gave 12·1 c.c. $N_2$ at 16° and 750 mm. $N=17·3$.

$C_8H_{18}ON_2$ requires $N=17·7$ per cent.

### α-*Propylbutyryl*-δ-*heptylcarbamide*, $CHPr_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CHPr_2$.

0·5 Gram of δ-carbimidoheptane and 0·5 gram of α-propylvaleramide were gradually heated together over a small flame under reflux to 200°; the liquid was then allowed to cool and recrystallised from alcohol, when 0·5 gram of the mixed carbamide melting at 89—90° was obtained in small prisms:

0·1240 gave 0·3066 $CO_2$ and 0·1276 $H_2O$. $C=67·4$; $H=11·5$.

0·1160 „ 10·2 c.c. $N_2$ at 22° and 744 mm. $N=10·0$.

$C_{16}H_{32}O_2N_2$ requires $C=67·5$; $H=11·3$; $N=9·9$ per cent.

It is insoluble in water, readily soluble in cold alcohol, and very readily so in ether or hot alcohol.

### *α-Propylvalerobromoamide* (1 *mol.*) *and Sodium Methoxide* (1 *mol.*). *Formation of Methyl δ-Heptylcarbamate*, $CHPr_2 \cdot NH \cdot CO_2Me$.

3·3 Grams of α-propylvalerobromoamide were suspended in 10 c.c. of methyl alcohol, and a solution of 0·35 gram of sodium in 5 c.c. of methyl alcohol was added at once at the room temperature. The liquor at once became clear, then hot, and began to boil. After boiling for another half-an-hour under reflux, the methyl alcohol was distilled off, and the residue diluted with water. This caused the separation of *methyl δ-heptylcarbamate* as an oil, which quickly became crystalline and then melted at 42°. This product distilled completely at 223° under normal pressure, and solidified on cooling, forming needles, which melted at 45—46° (corr.). 2·0 Grams of the distilled product were obtained, that is, 79 per cent. of the theoretical:

0·1240 gave 0·2832 $CO_2$ and 0·1234 $H_2O$. C=62·3; H=11·1.
$C_9H_{19}O_2N$ requires C=62·4; H=11·0 per cent.

It is insoluble in water, but very readily soluble in alcohol or ether.

*Ethyl δ-heptylcarbamate*, $CHPr_2 \cdot NH \cdot CO_2Et$, was similarly prepared in 80 per cent. yield, using sodium ethoxide in ethyl-alcoholic solution. It distils at 230—231° under normal pressure, and melts at 29—30° (corr.):

0·1358 gave 0·3218 $CO_2$ and 0·1366 $H_2O$. C=64·6; H=11·3.
$C_{10}H_{21}O_2N$ requires C=64·1; H=11·3 per cent.

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## LXXXVIII.—*Constitution of Aliphatic Diazo-compounds.*

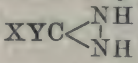
By Martin Onslow Forster and David Cardwell.

Nearly two years have elapsed since Thiele (*Ber.*, 1911, **44**, 2522) advocated a suggestion thrown out from time to time by others, to the effect that diazomethane and hydrazoic acid should be regarded as having the structure:

$$CH_2\vdots N\colon N \text{ and } HN\vdots N\colon N$$

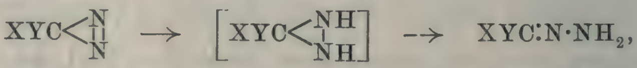
respectively, instead of the cycloid types hitherto accepted. Fresh evidence in favour of these formulæ was not put forward at the time, nor has it appeared since, and as this claim has been obediently admitted by other workers, there is no little danger that an idea fundamentally altering our conception of quinquevalent nitrogen should be allowed, prematurely, to be embraced as a fact.

The question of the azoimide nucleus was discussed by one of us in a paper presented to the VIIIth International Congress of Applied Chemistry, and it is therefore unnecessary to deal with this branch of the problem in the present communication. It is worth while to point out, however, that the cardinal objection to Thiele's formula for azoimides remains unanswered. Whilst it is true that certain compounds may be represented by formulæ in which quinquevalent nitrogen is non-ionisable, such as dimethylaniline oxide, $C_6H_5\cdot N(CH_3)_2:O$, and *N*-alkyl oxime ethers, $X\cdot CH:NY:O$, certainly no case is known in which quinquevalent nitrogen is satisfied by the equivalent of a single element or of groups having the same polarity. A formula which does violence to existing conceptions of this important element must first be based on the clearest possible evidence.

The claim to represent aliphatic diazo-compounds in the manner indicated is associated with the structure of condensation products from hydrazine and carbonyl derivatives, which must now be definitely accepted as that of hydrazones, $XYC:N\cdot NH_2$, rather than hydrazi-compounds,  $XYC{<}\substack{NH\\|\\NH}$ (Forster and Zimmerli, T., 1910, **97**, 2156; Staudinger and Kupfer, *Ber.*, 1911, **44**, 2197; Thiele, *loc. cit.*; and Wolff, *Annalen*, 1912, **394**, 23). Thiele argues that the facility of conversion between hydrazones and diazo-compounds:

$$XYC:N\cdot NH_2 \rightleftharpoons XYC:N\vdots N,$$

favours his formula and excludes the cycloid. He ignores the possible operation of the Hofmann-Curtius reaction, which, as already indicated (T., 1910, **97**, 2162) supplies an adequate explanation. The suggestion that chemical reaction should attack always the azo-group does not appear very cogent, because although reduction probably does attack it, forming a cycloid so unstable that it passes forthwith to the hydrazone:



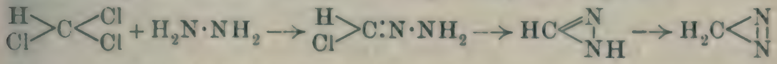
$$XYC{<}\substack{N\\ \|\\ N} \longrightarrow \left[XYC{<}\substack{NH\\|\\NH}\right] \longrightarrow XYC:N\cdot NH_2,$$

the great activity of aliphatic diazo-compounds in other respects may be explained by the tendency of a three-atom ring to undergo disruption under chemical influence.

The contribution to this question by Staudinger and Kupfer (*Ber.*, 1912, **45**, 501), although bringing to light a simple and convenient method of preparing diazomethane, is not convincing from a theoretical point of view. Instead of the course represented by them, namely:

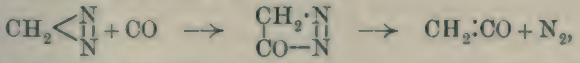
$$H_2N\cdot NH_2 + CHCl_3 + 3KOH \longrightarrow {>}C{:}N\cdot NH_2 + 3KCl + 3H_2O,$$
$${>}C{:}N\cdot NH_2 \longrightarrow H_2C{:}N\cdot N,$$

it is quite probable that the following changes take place:



$${}^{H}_{Cl}{>}C{<}^{Cl}_{Cl} + H_2N\cdot NH_2 \longrightarrow {}^{H}_{Cl}{>}C{:}N\cdot NH_2 \longrightarrow HC{<}\begin{array}{l}N\\|\\NH\end{array} \longrightarrow H_2C{<}\begin{array}{l}N\\\|\\N\end{array}$$

The production of keten from diazomethane and carbon monoxide might arise from an unstable cycloid:



$$CH_2{<}\begin{array}{l}N\\\|\\N\end{array} + CO \longrightarrow \begin{array}{l}CH_2\cdot N\\|\quad\;\;\|\\CO-N\end{array} \longrightarrow CH_2{:}CO + N_2,$$

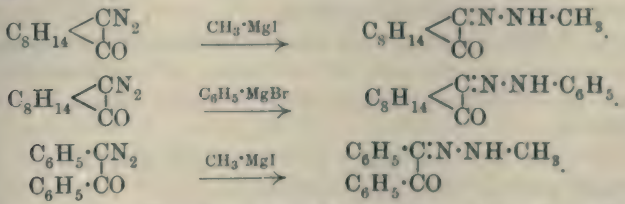
instead of by the alternative process:

$$CH_2{:}N{:}N + CO \longrightarrow CH_2{:}N\cdot N{:}CO \longrightarrow CH_2{:}CO + N_2,$$

the former series being in agreement with several changes of diazomethane too well known to be quoted again.

The more recent investigations of Darapsky and Prabhakar (*Ber.*, 1912, **45**, 1654, 2617) into the reduction of diazoacetic ester, although confirming the hydrazone structure for the initial product of this action, do not elucidate the constitution of the original material; moreover, it is noteworthy that Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3022), examining the absorption spectra of typical diazo-compounds, have found no justification for replacing the cycloid by Thiele's formula.

From the foregoing remarks it should be clear that more evidence must be produced before a final conclusion on this question can be drawn. We have therefore studied the effect of the Grignard reaction on diazocamphor and on diazodeoxybenzoin, those two compounds being selected as likely to yield readily identified products. Magnesium methyl iodide and magnesium phenyl bromide were used, and three of the four changes proceeded quite smoothly, yielding the corresponding substituted hydrazone of the original diketone:



$$C_8H_{14}{<}\begin{array}{l}CN_2\\|\\CO\end{array} \xrightarrow{CH_3\cdot MgI} C_8H_{14}{<}\begin{array}{l}C{:}N\cdot NH\cdot CH_3.\\|\\CO\end{array}$$
$$C_8H_{14}{<}\begin{array}{l}CN_2\\|\\CO\end{array} \xrightarrow{C_6H_5\cdot MgBr} C_8H_{14}{<}\begin{array}{l}C{:}N\cdot NH\cdot C_6H_5.\\|\\CO\end{array}$$
$$\begin{array}{l}C_6H_5\cdot CN_2\\\qquad\;|\\C_6H_5\cdot CO\end{array} \xrightarrow{CH_3\cdot MgI} \begin{array}{l}C_6H_5\cdot C{:}N\cdot NH\cdot CH_3.\\\qquad\;|\\C_6H_5\cdot CO\end{array}$$

The action of magnesium phenyl bromide on diazodeoxybenzoin, although, as will be seen later, pointing in the same direction, is much more complicated, involving these materials in the molecular proportion of 3: 2, and accompanied by elimination of benzophenone, which appears in the form of triphenylcarbinol:

$$2C_{14}H_{10}ON_2 + 3C_6H_5{\cdot}H = C_{19}H_{16}O + C_{27}H_{22}ON_4.$$

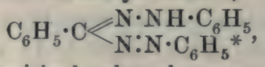
The nitrogenous product, $C_{27}H_{22}ON_4$, is a very remarkable compound, crystallising in silky, deep-red needles, and forming intensely coloured solutions in organic media, with which it shows a tendency to unite. Hydrogen chloride combines with it in a single molecular proportion, forming a pale buff hydrochloride, which is slowly dissociated by a large quantity of cold water. Acetic anhydride forms the usual deep red solution, which gradually fades, owing to production of a pale yellow monoacetyl derivative, which is rapidly hydrolysed by alcoholic alkali regenerating the original material. Although an acetone solution of potassium permanganate is decolorised immediately, the product could not be identified, but the action of ferric chloride is very definite, leading to 1 : 4-diphenyl-1 : 2 : 3 : 5-tetrazole (Wedekind, *Ber.*, 1896, **29**, 1854; Dimroth, *Ber.*, 1907, **40**, 2402), in association with benzoic acid; as the tetrazole contains only one phenyl group attached to nitrogen, the other being combined with an atom of carbon, it would appear that unless the Grignard agent has added phenyl to carbon, it has not added more than one such group to the original molecule, which must therefore contain the residue of both diazodeoxybenzoin molecules involved in the above equation. That it contains a benzoyl group is indicated by the fact that ethyl benzoate is produced when the alcoholic solution is boiled with hydrochloric acid, as also by the circumstance that benzoic acid accompanies the diphenyltetrazole in the ferric chloride oxidation.

Whilst the action of acetic anhydride indicates the presence of hydroxylic oxygen, it was not overlooked that this might arise from a process of enolisation brought about by the agent, and it was therefore necessary to ascertain whether the red substance is ketonic. The action of hydroxylamine acetate, however, which was studied from this point of view, unexpectedly gave rise to 2 : 5-diphenyl-1 : 3 : 4-triazole (Pinner, *Annalen*, 1897, **297**, 255), indicating a very profound disruption of the molecule.

Taking all the circumstances into consideration, we suggest that the red substance produced by the action of magnesium phenyl bromide on diazodeoxybenzoin is a formazyl derivative of the constitution,

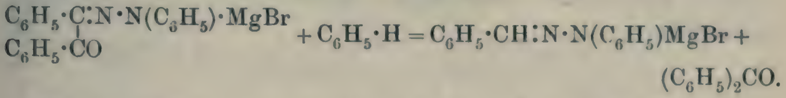
$$C_6H_5{\cdot}NH{\cdot}N{:}C(C_6H_5){\cdot}N{:}N{\cdot}CH(C_6H_5){\cdot}CO{\cdot}C_6H_5,$$

a substance derived from formazylbenzene,



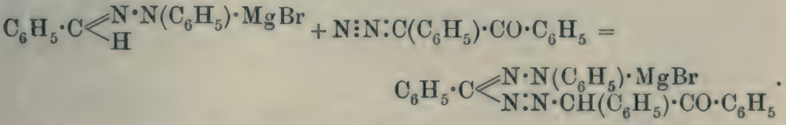
$$C_6H_5{\cdot}C\Big\langle\begin{matrix}N{\cdot}NH{\cdot}C_6H_5\\ N{:}N{\cdot}C_6H_5{}^*\end{matrix},$$

by replacing the asterisked phenyl group with a deoxybenzoin residue. The production of such a compound might be explained by supposing that the magnesium derivative of benzilphenylhydrazone expected to arise from the initial action of magnesium phenyl bromide on diazodeoxybenzoin changed, under the influence of the Grignard agent, into the magnesium derivative of benzylidenephenylhydrazone and benzophenone:



$$\begin{array}{l}C_6H_5\cdot C{:}N\cdot N(C_6H_5)\cdot MgBr\\ \quad\; | \\ C_6H_5\cdot CO\end{array} + C_6H_5\cdot H = C_6H_5\cdot CH{:}N\cdot N(C_6H_5)MgBr + (C_6H_5)_2CO.$$

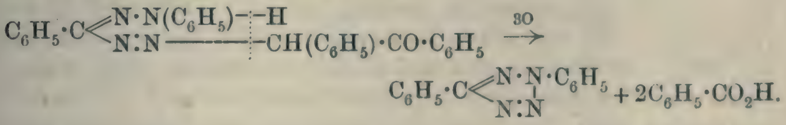
The magnesium compound must then be attacked by diazodeoxybenzoin, yielding the magnesium derivative of the red substance, just as a diazonium salt produces a formazyl derivative from benzylidenephenylhydrazone itself:



$$C_6H_5\cdot C{<}\begin{array}{l}N\cdot N(C_6H_5)\cdot MgBr\\ H\end{array} + N{:}N{:}C(C_6H_5)\cdot CO\cdot C_6H_5 = C_6H_5\cdot C{<}\begin{array}{l}N\cdot N(C_6H_5)\cdot MgBr\\ N{:}N\cdot CH(C_6H_5)\cdot CO\cdot C_6H_5\end{array}.$$

It appears to be necessary to present the benzylidenephenylhydrazone in the form of its magnesium derivative, because the substance itself, when left in ether with diazodeoxybenzoin, does not yield the formazyl derivative; moreover, the latter does not arise from diazodeoxybenzoin and benzilphenylhydrazone under the same conditions.

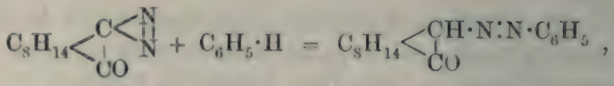
Although it is difficult to explain the production of diphenyltriazole by the action of hydroxylamine on the formazyl derivative, oxidation by ferric chloride with elimination of benzoic acid is a comparatively simple step, involving removal of the deoxybenzoin nucleus in association with hydrogen:



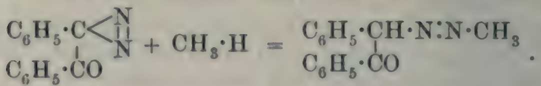
$$C_6H_5\cdot C{<}\begin{array}{l}N\cdot N(C_6H_5)-\vdots-H\\ N{:}N\text{———————}\vdots-CH(C_6H_5)\cdot CO\cdot C_6H_5\end{array} \xrightarrow{3O} C_6H_5\cdot C{<}\begin{array}{l}N\cdot N\cdot C_6H_5\\ \quad\;\, |\\ N{:}N\end{array} + 2C_6H_5\cdot CO_2H.$$

The remaining properties of the substance, notably its intense red colour, are in agreement with the suggested classification as a formazyl derivative.

Returning now to the original problem, namely, the constitution of the aliphatic diazo-compounds, it must be admitted that the action of the Grignard agents on diazocamphor and diazodeoxybenzoin strongly favours the Thiele formula in preference to the cycloid. It was expected that if the latter truly represents the constitution of diazomethane, its derivatives would lead to azo-compounds, thus:

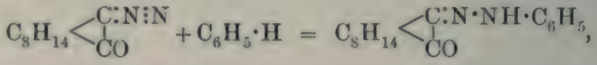


$$C_8H_{14}<\begin{matrix}C<\begin{matrix}N\\ \|\\ N\end{matrix}\\ |\\ CO\end{matrix} + C_6H_5\cdot H = C_8H_{14}<\begin{matrix}CH\cdot N{:}N\cdot C_6H_5\\ |\\ CO\end{matrix},$$



$$\begin{matrix}C_6H_5\cdot C<\begin{matrix}N\\ \|\\ N\end{matrix}\\ |\\ C_6H_5\cdot CO\end{matrix} + CH_3\cdot H = \begin{matrix}C_6H_5\cdot CH\cdot N{:}N\cdot CH_3\\ |\\ C_6H_5\cdot CO\end{matrix}.$$

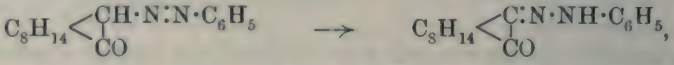
The alternative constitution should lead to substituted hydrazones:



$$C_8H_{14}<\begin{matrix}C{:}N{:}N\\ |\\ CO\end{matrix} + C_6H_5\cdot H = C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot C_6H_5\\ |\\ CO\end{matrix},$$

the course actually followed by the experiments.

We believe that this is the best evidence yet furnished for Thiele's formula, but there is one objection to it, namely, the uncertainty whether the azo-compound which should be produced from the cycloid diazo-derivative is capable of separate existence. It seems quite probable that such a substance would change to the isomeric substituted hydrazone:



$$C_8H_{14}<\begin{matrix}CH\cdot N{:}N\cdot C_6H_5\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot C_6H_5\\ |\\ CO\end{matrix},$$

because the latter substance is produced instead of the former when a diazonium salt acts on the sodium salt of camphorcarboxylic acid or hydroxymethylenecamphor; on the other hand, there has been described a benzeneazodeoxybenzoin distinct from benzilphenylhydrazone, so that in this case at least there should be no reason for the azo-compound to change into the phenylhydrazone, but then this is the very case which is complicated by the production of the formazyl derivative.

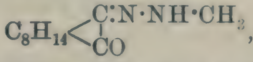
In conclusion, it should be mentioned that the methylhydrazone of camphorquinone has been obtained in two stereoisomeric forms, the colourless $\alpha$-derivative melting at 133—134° and having $[\alpha]_D$ 367·5°, and the yellow $\beta$-derivative, which melts at 46°, has $[\alpha]$ 296°, and changes into the stable modification when heated. These two forms of camphorquinonemethylhydrazone are strictly comparable with the pairs of hydrazones, semicarbazones, and phenylhydrazones of camphorquinone already described (Forster and Zimmerli, T., 1910, **97**, 2156; 1911, **99**, 478).

## EXPERIMENTAL.

### *Action of Grignard Agents on Diazocamphor.*

Three grams of diazocamphor dissolved in 25 c.c. of dry ether was gradually added to the cooled Grignard agent prepared from 5 grams of methyl iodide and 0·8 gram of magnesium in 50 c.c. of dry ether; the additive product separated as a greyish, semi-solid mass without liberation of nitrogen, and was decomposed with ice and ammonium chloride. On evaporating the ether by a current of air, colourless needles remained embedded in a small proportion of oil, the latter being removed by cold petroleum; the solid product was readily soluble in benzene, from which it was precipitated by petroleum in needles melting at 133—134°, identical with camphorquinone-α-methylhydrazone (see below):

0·0980 gave 13·1 c.c. $N_2$ at 24° and 766 mm. N = 15·0.
$C_{11}H_{18}ON_2$ requires N = 14·4 per cent.

*Camphorquinone-α-methylhydrazone,*  $C_8H_{14}\Big<\begin{matrix}C:N\cdot NH\cdot CH_3\\ | \\ CO\end{matrix}$, was prepared by shaking during four hours, 6 grams of camphorquinone in 10 c.c. of alcohol with 16 grams of methylhydrazine sulphate and the quantity of concentrated aqueous sodium hydroxide necessary to liberate the base; after remaining twelve hours at 40°, the liquid was diluted with water, which precipitated the methylhydrazone, freely soluble in cold organic media excepting petroleum. A solution containing 0·2600 gram in chloroform diluted to 25 c.c. gave $\alpha_D$ 11°28′ in a 3-dcm. tube, whence $[\alpha]_D$ 367·5°, falling to 295·0° in the course of five weeks.

*Camphorquinone-β-methylhydrazone* arose from the colourless modification on passing a current of steam through a suspension in 10 per cent. aqueous potassium hydroxide, being extracted from the distillate by ether; when this was dried and evaporated, some unchanged α-modification was deposited, but extraction with cold petroleum (b. p. 40—50°) removed the new isomeride, which is freely soluble, separating on spontaneous evaporation in hard, transparent, pale yellow crystals, melting at 46°:

0·1232 gave 15·0 c.c. $N_2$ at 20° and 756 mm. N = 14·2.
$C_{11}H_{18}ON_2$ requires N = 14·4 per cent.

A solution containing 0·2779 gram in chloroform diluted to 25 c.c. gave $\alpha_D$ 9°52′ in a 3-dcm. tube, whence $[\alpha]_D$ 295·9°, falling to 262·4° in the course of four months.

This modification must be regarded as the unstable form, because it changes slowly into the less fusible isomeride when preserved in the sulphuric acid desiccator, although resisting this alteration when calcium chloride alone is present; moreover, when hydrogen chloride is passed into an ethereal solution, the colourless hydrochloride which is precipitated yields the α-methylhydrazone when treated with sodium carbonate. Thus the physical characteristics of the two methylhydrazones are in precise agreement with the respective members of the series already described (*loc. cit.*).

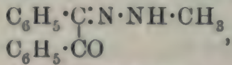
When diazocamphor was treated with magnesium phenyl bromide, the additive compound again separated without liberation of gas, and on decomposition with water yielded camphorquinone-α-phenylhydrazone.

### *Action of Magnesium Methyl Iodide on Diazodeoxybenzoin.*

Diazodeoxybenzoin is best prepared from benzilhydrazone by agitating a suspension in dry ether with yellow mercuric oxide, the readiness with which the solvent evaporates leading to a more easily purified product than when benzene is employed. Three grams in 25 c.c. of ether was added to the Grignard agent prepared from 5 grams of methyl iodide and 0·8 gram of magnesium in 50 c.c. of ether. The additive compound was brown, and, on proceeding in the usual manner, 2 grams of crystalline material was obtained, precipitated by petroleum from a benzene solution in colourless needles, melting at 138°, not depressed by admixture with benzilmethylhydrazone (see below):

0·1546 gave 16·1 c.c. of $N_2$ at 20° and 770 mm. N = 12·1.

$C_{15}H_{14}ON_2$ requires N = 11·8 per cent.

*Benzilmethylhydrazone*,  $\begin{array}{l} C_6H_5\cdot C{:}N\cdot NH\cdot CH_3 \\ C_6H_5\cdot CO \end{array}$, prepared by heating 5 grams of benzil in 10 c.c. of alcohol with 7 grams of methylhydrazine sulphate and 6·5 grams of potassium hydroxide in 20 c.c. of water during six hours under reflux, is readily soluble in organic media excepting petroleum, but is insoluble in water.

### *Action of Magnesium Phenyl Bromide on Diazodeoxybenzoin.*

On adding an ethereal solution of the diazo-compound (3 grams) to the Grignard agent prepared from bromobenzene (5 grams) and magnesium (0·8 gram), the first few drops developed an intense, purple coloration, changing with more material to a brilliant blue-black, and becoming once more purple at the close of the action. The additive product was brownish-purple, and when decomposed with ice and ammonium chloride, yielded a dark red ethereal solution, leaving the water colourless. On evaporation, the oily residue soon deposited crystals, which were drained from bromobenzene and rubbed with a small quantity of methyl alcohol; this removed triphenylcarbinol, leaving a dark red product, which crystallised from much hot methyl alcohol in cinnabar needles, melting at 152°:

0·1375 gave 0·3888 $CO_2$ and 0·0693 $H_2O$. C = 77·1; H = 5·6.
0·1196 „ 13·8 c.c. $N_2$ at 20° and 760 mm. N = 13·5.

$C_{27}H_{22}ON_4$ requires C = 77·5; H = 5·3; N = 13·4 per cent.

The substance displays a tendency to combine with organic solvents; for instance, in benzene it first dissolves, and then separates in bulky crystals, soluble in a further quantity of the hydrocarbon, forming a damson-coloured solution, from which petroleum precipitates silky, red needles. It sometimes happens that the deposit from the original ethereal solution is dark brown, and we believe that this is due to bromobenzene of crystallisation, because the brown crystals retained their colour when rubbed with cold methyl alcohol, but formed a dark red solution in much hot methyl alcohol, the cinnabar needles deposited therefrom becoming brown again when treated with hot bromobenzene.

On treating a very dilute solution in cold alcohol with a few drops of aqueous sodium hydroxide, the clear, pale red liquid becomes intensely claret-coloured, but dilution with much water restores the original red colour. The solution in concentrated sulphuric acid is deep red, becoming emerald green with a very small proportion of water, further dilution precipitating a pale brown, amorphous substance which has not been identified. With ammoniacal silver oxide, the alcoholic solution gives a greenish-yellow precipitate, but silver is not deposited even when the solution is boiled; similarly, mercury acetamide is not reduced, but yields a flocculent, yellow precipitate.

*The Hydrochloride.*—When rubbed with cold dilute hydrochloric acid, the red substance became pale yellow, the colour being restored by alcohol or much water. On passing dry hydrogen chloride into an ethereal solution, this rapidly became colourless, depositing a pale buff powder, which began to darken at about 140°, and decomposed at the melting point of the original material:

0·1805 gave 0·0562 AgCl. Cl = 7·7.

$C_{27}H_{22}ON_4,HCl$ requires Cl = 7·8 per cent.

In absolute alcohol the hydrochloride forms a pale yellow solution, but on adding water the red colour is immediately developed, owing to removal of hydrogen chloride.

*The Acetyl Derivative.*—On dissolving the red substance in hot acetic anhydride, the colour fades rapidly, and the same change occurs more slowly when the solid remains suspended in the agent during four hours at 40°; on shaking the pale yellow solution with water a yellow solid is slowly produced, but although freely soluble in alcohol, benzene, acetone, or ethyl acetate and sparingly soluble in cold petroleum, it could not be crystallised. The amorphous material melted at 99°:

0·0526 gave 5·6 c.c. $N_2$ at 20° and 755 mm. N = 12·3.

$C_{27}H_{21}ON_4Ac$ requires N = 12·2 per cent.

$C_{27}H_{20}ON_4Ac_2$ „ N = 11·2 „

The acetyl derivative resists the action of boiling water, but rapidly develops a red coloration with alcoholic alkali, clearly indicating a hydrolysable acetyl derivative as distinguished from an acetate.

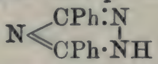
*Action of Ferric Chloride.*—On adding aqueous ferric chloride to an alcoholic solution of the red substance, the colour faded rapidly, ferrous salt being recognisable in the liquid; water precipitated a flocculent material, which was crystallised first from diluted alcohol and finally from petroleum, when it melted at 101·5—102°:

0·1243 gave 0·3201 $CO_2$ and 0·0553 $H_2O$. C = 70·2; H = 4·9.
0·1213 „ 25·8 c.c. $N_2$ at 20° and 768 mm. N = 25·2.
$C_{13}H_{10}N_4$ requires C = 70·3; H = 4·5; N = 25·2 per cent.

This formula and the properties of the compound identify it with 1 : 4-diphenyl-1 : 2 : 3 : 5-tetrazole, which was obtained by oxidising the tetrazolium chloride derived from *p*-hydroxyformazylbenzene (Wedekind, *loc. cit.*). The aqueous alcoholic filtrate from the precipitated diphenyltetrazole was found to contain benzoic acid, indicating the presence of a benzoyl group in the original compound.

*Action of Hydroxylamine.*—An alcoholic solution of the red substance was heated with aqueous hydroxylamine acetate during four hours under reflux, when the colour faded, and water precipitated a pale brown material; this, when dry, was treated with small quantities of cold benzene, which removed a freely soluble, intensely brown, fluorescent product, which was not identified. The residue dissolved very readily in cold methyl alcohol, separating on addition of water in lustrous needles, which changed to transparent plates; in the desiccator the crystals became opaque, and then melted at 191°:

0·1051 gave 0·2927 $CO_2$ and 0·0490 $H_2O$. C = 75·9; H = 5·2.
0·1117 „ 18·3 c.c. $N_2$ at 20° and 760 mm. N = 19·2.
$C_{14}H_{11}N_3$ requires C = 76·0; H = 5·0; N = 19·0 per cent.

The formula and properties of this product agree with those of 2 : 5-diphenyl-1 : 3 : 4-triazole,  $N\Big\langle\begin{array}{l}CPh{:}N\\ \quad\;\;|\\ CPh{\cdot}NH\end{array}$, which was identified further by conversion into the acetyl derivative melting at 105°.

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# LXXXIX.—*The Conversion of Sodium Hydrosulphide into Sodium Monosulphide.*

By John Smeath Thomas and Alexander Rule.

In a previous paper (T., 1911, **99**, 558) one of us described the action of hydrogen sulphide on the alkyloxides of sodium and potassium in alcoholic solution. This action affords a simple method of obtaining the pure anhydrous hydrosulphides of those metals.

One of the objects of the present investigation was to ascertain if a reaction analogous to that made use of in the preparation of sodium monosulphide in aqueous solution took place between sodium hydrosulphide and sodium ethoxide according to the equation:

$$C_2H_5{\cdot}ONa + NaHS = C_2H_5{\cdot}OH + Na_2S.$$

The preparation of the anhydrous monosulphide of sodium in a state of purity appears to be a matter of considerable difficulty. Hugot (*Compt. rend.*, 1899, **129**, 388) describes the preparation by the action of sodium on sulphur in liquid ammonia, the product being a white, amorphous solid. Böttger (*Annalen*, 1884, **223**, 355) and others describe the preparation of the anhydrous monosulphide by dehydrating the hydrated substance in a current of hydrogen. This method has been repeated by the authors of the present paper, and it is found to be quite unsuitable, as the product is always brown, and gives a precipitate of sulphur when treated with hydrochloric acid. In view of our investigations concerning the action of heat on sodium hydrosulphide, the colour of the above product may be explained as due to the partial hydrolysis of the monosulphide by the water derived from the decomposition of the hydrate, and the subsequent dissociation of sodium hydrosulphide produced, with the formation of hydrogen sulphide.

When equimolecular quantities of sodium ethoxide and sodium hydrosulphide are mixed together under varying conditions, it is found that the reaction mentioned above is never complete, sodium ethoxide always being present to some extent in the final product.

By increasing the concentration of one of the components, namely, the ethoxide, it is possible, however, to convert the hydrosulphide completely into the monosulphide.

It must therefore be concluded that the reaction:

$$C_2H_5{\cdot}ONa + NaHS = Na_2S + C_2H_5{\cdot}OH,$$

is reversible, and that sodium monosulphide in alcoholic solution undergoes alcoholysis, analogous to the hydrolysis that takes place in aqueous solution.

Owing to the difficulty of separating the mixture of monosulphide and ethoxide without loss of the former, the reaction does not form a convenient method for the preparation of sodium monosulphide.

The action of heat on the hydrosulphide is interesting, for, starting with the anhydrous hydrosulphide, it should, theoretically, be possible to bring about the dissociation of that compound, thus:

$$2NaHS = Na_2S + H_2S.$$

The authors find that this simple change can be effected, but that under ordinary conditions it is complicated by a secondary reaction.

When either sodium or potassium hydrosulphide is heated in the air it becomes yellow below 100°, and as the temperature is raised, the substance darkens in colour, until finally it fuses to a very dark red liquid. On cooling, the order of change of colour is reversed, but the cold solid is always yellow, and always contains polysulphide sulphur. This colour change also takes place when the hydrosulphide is heated rapidly in a vacuum, or in an atmosphere of hydrogen or hydrogen sulphide.

As a result of the experiments described below, the authors attribute the coloration entirely to the action of sulphur produced by the dissociation of hydrogen sulphide, the latter being derived from the dissociation, in the first place, of the hydrosulphide. The hydrosulphides are readily acted on by sulphur with the formation of polysulphides which possess intense colouring power, a mere trace of sulphur being sufficient to bring about a distinct coloration of an alcoholic solution of the hydrosulphide.

Analysis of the mass obtained after rapidly heating the hydrosulphide to fusion and allowing to cool shows that the composition of the substance is not greatly changed, but the small amount of polysulphide which is always present is sufficient to account for the intense yellow colour of the products.

In every case hydrogen sulphide is a product of the action of heat, and can be readily recognised. It is therefore difficult to understand the statement made by Bloxam (T., 1900, **77**, 753) in connexion with potassium hydrosulphide, that the latter compound is stable towards heat, and will bear comparison with its oxygen analogue, potassium hydroxide.

In the case of sodium hydrosulphide our experiments show that the compound exhibits a distinct dissociation pressure at temperatures considerably below its melting point. By heating it in a vacuum with gradual rise of temperature and continuous removal of the hydrogen sulphide evolved, it has been found possible to bring about complete dissociation of the hydrosulphide into the monosulphide in the sense of the equation:

$$2NaHS = Na_2S + H_2S.$$

Although under these conditions the dissociation of hydrogen sulphide is increased, the extent of the secondary reaction mentioned above is rendered negligible, as the concentration of the gaseous phase is always exceedingly low.

## EXPERIMENTAL.

### *Mixture of Equimolecular Proportions of Sodium Ethoxide and Sodium Hydrosulphide in Alcoholic Solution.*

### *Solution Allowed to Crystallise in a Vacuum.*

One gram of sodium was dissolved in 20 c.c. of absolute ethyl alcohol, and the solution saturated with hydrogen sulphide. The excess of hydrogen sulphide was removed by warming on the water-bath and passing a rapid current of hydrogen through the solution. The solution of sodium hydrosulphide obtained in this way was treated with a solution of sodium ethoxide prepared by dissolving 1 gram of sodium in 20 c.c. of absolute alcohol. The mixture was kept in a vacuum over calcium chloride, and the crystalline crusts which separated were removed, washed with a little alcohol, and allowed to dry in a vacuum.

The product fused on heating to a dark yellow liquid. Alcohol was evolved, and a strong odour of mercaptan was emitted. On heating more strongly, partial charring took place. The substance behaved as a mixture of the hydrosulphide and the ethoxide, containing a certain amount of alcohol of crystallisation.

This method therefore does not yield the monosulphide, and it was discarded in favour of precipitation with ether, the method used in the preparation of the hydrosulphide (*loc. cit.*).

*Precipitation with Ether.*—The mixture of hydrosulphide and ethoxide was made up as described in the previous experiment. The mixture was boiled for two hours under reflux in a current of hydrogen, allowed to cool, and then poured into much dry ether. A white, crystalline precipitate was produced, which was collected, washed with ethyl alcohol and ether, and dried in a vacuum:

0·2815 gave 0·2560 $Na_2SO_4$. Na = 29·46.
0·4083 „ 0·8525 $BaSO_4$ S = 28·68.

The substance contained a considerable proportion of alcohol, which was evolved on heating.

Ratio Na : S in product = 1 : 0·9735.
Ratio Na : S in NaHS = 1 : 1·3913.
Ratio Na : S in $Na_2S$ = 1 : 0·6956.

According to these figures, the product consisted of a mixture of hydrosulphide and monosulphide in nearly equimolecular proportions, together with a certain amount of alcohol.

A series of experiments was carried out in which the relative amount of sodium ethoxide to one gram-molecule of hydrosulphide was varied from one to three gram-molecules. Alcohol was removed from the solution by evaporation in a rapid current of hydrogen until solid just began to separate on the sides of the vessel. The solution was then poured into ether, and the product collected, washed with alcohol in order to remove sodium ethoxide as far as possible, then dried in a vacuum and analysed. The figures indicated that the proportion of sodium monosulphide gradually increased until when three gram-molecules of ethoxide were present a product was obtained which gave the following results on analysis:

0·3646 gave 0·4183 $Na_2SO_4$. Na = 37·16.
0·3444 „ 0·6412 $BaSO_4$. S = 25·56.
Alcohol (diff.) = 37·28

$Na_2S,C_2H_6O$ requires Na = 37·09; S = 25·81; $C_2H_6O$ = 37·09 per cent.

On heating the substance, which was evidently an alcoholate of sodium monosulphide, alcohol was evolved, and a residue remained, which darkened slightly on further heating, but did not fuse when heated to redness.

A portion of the alcoholate was placed in a flask connected with a Töpler pump, and the vessel was exhausted. The flask was then heated in an oil-bath to 150°, the alcohol being removed continually by absorbing it with phosphoric oxide. A product was obtained which was very faintly buff-coloured, but dissolved in water forming a clear solution, and in hydrochloric acid forming a very slightly opalescent solution. It did not fuse when heated to redness:

0·2931 gave 0·5318 $Na_2SO_4$. Na = 58·77.
0·3360 „ 0·9953 $BaSO_4$. S = 40·68.
$Na_2S$ requires Na = 58·97; S = 41·03 per cent.

The yield of sodium monosulphide was only small, as it was found necessary to wash the product of precipitation several times with alcohol in order to free it completely from ethoxide, and this occasioned considerable loss of the sulphide.

### *The Action of Heat on Sodium Monosulphide.*

The following experiments were carried out by heating pure anhydrous sodium hydrosulphide, contained in a small distillation flask, in a bath of sulphuric acid, and, finally, to fusion in a bath of molten solder.

1. *In Dry Air at Atmospheric Pressure.*—The substance became slightly yellow at about 80°. Between 100° and 105° the colour deepened rapidly to orange-yellow. On further heating, the sub-

stance became darker, and finally fused to an almost black liquid at about 350°.

Hydrogen sulphide and sulphur dioxide were evolved during the heating, and the fusion, which on cooling became bright yellow, was immediately decomposed on treatment with hydrochloric acid, a copious precipitate of sulphur, derived partly from polysulphides and partly from oxidation compounds, being produced.

2. *In Dry Hydrogen at Atmospheric Pressure.*—The yellow coloration was again noticeable at 80°, and it became distinctly deeper between 100° and 105°, although not so intense as in the previous experiment. After the substance had fused, the gas in the flask was displaced by dry hydrogen, and was found to be rich in hydrogen sulphide. The fusion was decomposed on treatment with hydrochloric acid, giving a precipitate of sulphur, which, in this case, must have been derived entirely from the polysulphide formed. The polysulphide sulphur was estimated by decomposing a portion of the substance with dilute hydrochloric acid and weighing the precipitated sulphur in a Gooch crucible (Küster and Heberlein, *Zeitsch. anorg. Chem.*, 1905, **43**, 53):

1·1899 gave 0·0074 sulphur. Polysulphide sulphur = 0·62 per cent.

3. *In Dry Hydrogen Sulphide at Atmospheric Pressure.*—Similar colour changes. Analysis of the fusion showed that the amount of polysulphide sulphur was considerably greater in this case. This is to be expected, as the hydrogen sulphide forming the atmosphere is itself partly dissociated at the temperatures employed:

2·0426 gave 0·0365 sulphur. Polysulphide sulphur = 1·78 per cent.

4. *In a Vacuum.*—Sodium hydrosulphide contained in an exhausted flask, which was plunged into a bath of molten solder at 400°, became bright yellow and fused, with evolution of hydrogen sulphide, but when the heating was carried out gradually, the substance was completely dissociated into the monosulphide without the production of any yellow colour.

About 5 grams of freshly prepared pure sodium hydrosulphide were placed in a small Jena-glass flask connected to a Töpler pump, a tube of solid potassium hydroxide being interposed between the flask and the pump in order to absorb the hydrogen sulphide evolved. The flask was exhausted, and was then heated in an air-bath, the temperature of which was recorded by means of a thermometer filled with nitrogen. During the heating process the various changes in the appearance of the substance were carefully noted as the temperature was gradually raised. At 100° it acquired a peculiar greenish-yellow tinge, which first became noticeable round the edges of the substance, but gradually spread throughout the entire mass. At 180° the potassium hydroxide in the absorption tube became moist, indicating that hydrogen sulphide was being evolved. At 250° the evolution of hydrogen sulphide was comparatively rapid. The temperature of the bath was gradually raised to 500°, and was maintained there for two days. The substance, which was now pale brown, did not fuse at that temperature, but remained in the form of a powder. On cooling, a faintly buff-coloured product was obtained, which readily dissolved in water and alcohol, and gave a very faintly opalescent solution on treatment with hydrochloric acid:

0·2416 gave 0·4383 $Na_2SO_4$. Na = 58·76.
0·2892 „ 08754 $BaSO_4$. S = 41·57.
$Na_2S$ requires Na = 58·97; S = 41·03 per cent.

From the result of the analysis it is evident that the product is sodium monosulphide, and it is therefore possible to bring about the complete dissociation of the hydrosulphide at a temperature not exceeding 500°, and, by observing the conditions described, to avoid the secondary reaction which results in the formation of polysulphides.

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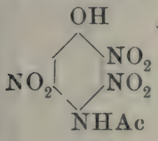
# XC.—*The Absorption Spectra of Some Derivatives of the Nitroaminophenols in Relation to their Constitution.*

By RAPHAEL MELDOLA and JOHN THEODORE HEWITT.

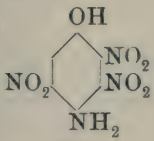
THE compounds of which the absorption spectra are described in the present paper have been selected for the special reason that they form a natural group, the members of which are comparable among themselves, and also because several of them show remarkable and visible colour changes under the influence of acids and alkalis respectively. With respect to the individual compounds dealt with, picramic acid (2:4-dinitro-6-aminophenol) and *iso*-picramic acid (2:6-dinitro-4-aminophenol) may be considered to have had their constitutions determined long ago so far as concerns the positions of the nitro- and the amino-groups with respect to the hydroxyl group. The methyl ether of *iso*picramic acid (2:6-dinitro-*p*-anisidine) was described by one of the authors and F. G. C. Stephens in 1905 (T., **87**, 1204). The hydroxyl group of picramic acid appears to be incapable of methylation directly or indirectly, and all attempts to prepare 2:4-dinitro-*o*-anisidine have hitherto failed. Of the two possible trinitro-derivatives of *p*-aminophenol only one is at present known, the acetyl derivative having been described by one of the authors in 1906 (T., **89**, 1935) and the trinitroaminophenol itself in 1909 (Meldola and Hay, T., **95**, 1379). Although only one of the two possible trinitro-*p*-aminophenols is known, both of the possible trinitroanisidines have been obtained (Reverdin and de Luc, *Arch. Sci. phys. nat.*, 1909, [iv], **27**, 383; Meldola and Kuntzen, T., 1910, **97**, 455), and their absorption spectra are given in the present paper.

With respect to the constitution of these trinitro-derivatives, it appears from new evidence which has recently been obtained by M. Reverdin that the formulæ of these compounds so far as concerns the position of the third nitro-group will require modification.

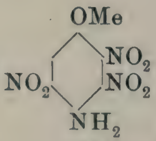
The original trinitroacetylaminophenol and trinitroaminophenol were assigned formulæ (I and II) representing them as 2:3:5-trinitro-derivatives:



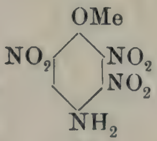
(I.)



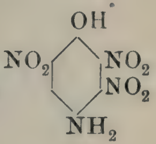
(II.)



(III.)



(IV.)



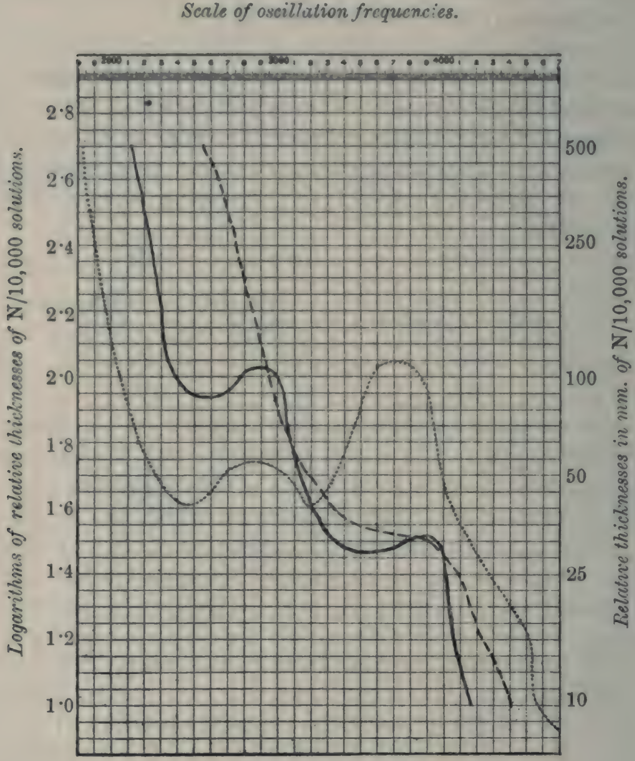
(V.)

The corresponding trinitroanisidine obtained by the methylation of I and hydrolysis of the acetyl derivative was accordingly given formula III, and the trinitroanisidine of Reverdin and de Luc the alternative formula IV. The evidence on which the 2:3:5-constitution was assigned to trinitroaminophenol, although indirect, was perfectly definite so far as it went. It appears, however, that during the nitration of some of these derivatives of *p*-aminophenol the passage to the trinitro-stage may be accompanied by a quite unsuspected migration of the third nitro-group, and that the trinitroanisidine of Reverdin and de Luc is in reality the 2:3:5-modification (III), whilst the isomeride is the 2:3:6-modification (IV). From this it follows that the known trinitroaminophenol is also the 2:3:6-modification (V), and that the isomeric 2:3:5-trinitroaminophenol (II) yet remains to be discovered. The evidence which has rendered this revision of the position of the third nitro-group will be submitted by one of the authors and M. Reverdin in a later communication, when the experiments bearing on this subject have been completed.

## *Absorption Spectra of Dinitroaminophenols and Trinitroanisidines.*

*Picramic Acid.*—This compound gives different spectra according to whether it is examined in alcohol alone, in alcohol to which hydrochloric acid has been added, or in dilute aqueous sodium hydroxide. Addition of hydrochloric acid to the alcoholic solution shifts the absorption to the ultra-violet end of the spectrum, whilst addition of sodium hydroxide causes the absorption to move in the direction of the red, the colour change which accompanies this shift taking place when the concentration of hydrogen ions in the solution lies between the limits of $10^{-2}$ and $10^{-3}$. Since the colour

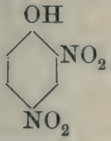
FIG. 1.

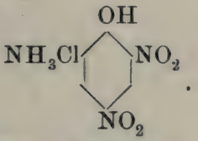


*Picramic acid:*
———— *In alcohol.* — — — *In alcoholic hydrochloric acid.*
………… *In aqueous sodium hydroxide.*

change for 2:4-dinitrophenol also occurs between the same limits, this substance and picramic acid have nearly the same dissociation constants.

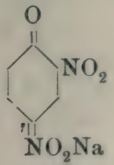
Comparison of the absorption spectra of picramic acid and 2:4-dinitrophenol is of interest. The latter compound gives a broad, shallow band with its head at an oscillation frequency of 3400 (Buttle and Hewitt, T., 1909, **95**, 1755) if, before photographing, the alcoholic solution is acidified with hydrochloric acid in order to restrain the ionisation of the phenol. In the case of picramic acid, the band no longer comes to a head, but the shape of the absorption curve shows that there is a chief oscillation frequency about 3400, the curve becoming practically flat at that point. Excess of hydrogen chloride being present in both cases, it may be assumed that the absorptions measured were those corresponding with the respective structures:



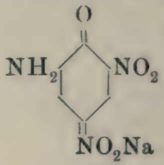


As is generally noticed, substitution of hydrogen by the ammonium chloride group, $NR_3Cl$ (here $R=H$ or alkyl; compare methyl-green, etc.), has very little influence on the absorption.

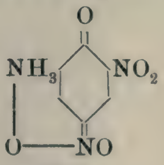
Addition of alkali has an even more marked effect on the absorption of picramic acid than on that of 2:4-dinitrophenol. In the latter case the head of the band (now well in the visible spectrum) is found at 2700, but with the introduction of an amino-group the shift is as far as oscillation frequency 2480. In these cases one is presumably dealing with salts having the constitutions I and II, or



(I.)



(II.)



(III.)

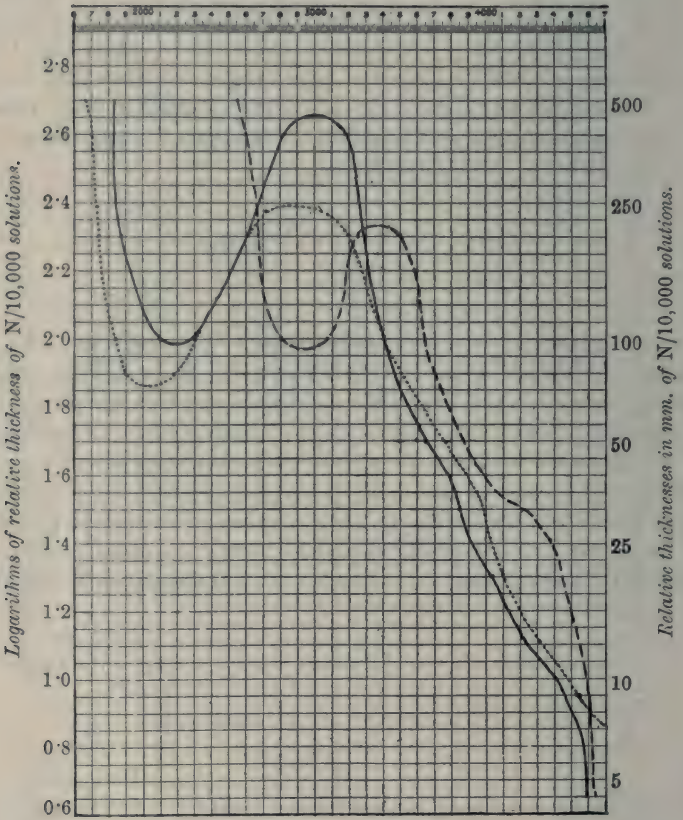
their respective ions, the "auxochromic" effect of the extra amino-group being quite pronounced. In alcoholic solution the picramic acid gives an absorption spectrum differing from that given either in acid or alkaline solution, although it resembles the latter more closely than the former. We are inclined to attribute to the acid, which is not likely to be dissociated very highly in alcoholic solution, a formula such as III, which represents it as an internal salt (compare Green and Rowe, this vol., p. 511).

iso*Picramic Acid.*—*iso*Picramic acid may be compared in a similar manner with 2:6-dinitrophenol, similar relationships as to oscillation frequency being observed in this case:

| | 2 : 6-Dinitrophenol | *iso*Picramic acid. |
|---|---|---|
| Alcohol + HCl ................... | 2950 | 2950 |
| Alcohol ........................... | — | 2200 |
| Aqueous NaOH.................... | 2300 | 2000 |

FIG. 2.

*Scale of oscillation frequencies.*

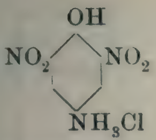


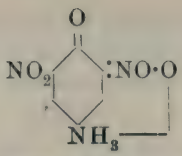
iso*Picramic acid:*

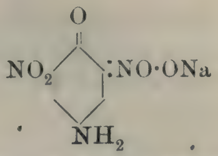
———— *In alcohol.* — — — *In alcoholic hydrochloric acid.*

............ *In aqueous sodium hydroxide.*

Arguments such as those which have been used for 2:4-dinitrophenol and picramic acid lead to the conclusion that the structures in acid, neutral, and alkaline solutions may be represented by the following formulæ:

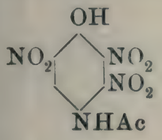


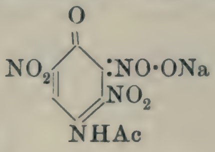




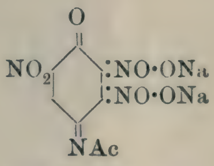
Although the absorption spectra in neutral solution and in excess of alkali do not appear very markedly different on the plotted diagram of absorption, the change is very striking to the eye, since, when the alkaline salt is formed, the yellow part of the spectrum is blotted out, and the colour changes from orange to a splendid purple-red. This property of the compound has suggested its utilisation as an indicator, for which purpose it appears to offer in some cases advantages over the indicators in general use (Meldola, Hale, and Thompson, *Chemical World*, 1912, **1**, 327). The change occurs when the concentration of hydrogen ions is reduced from $N \times 10^{-5}$ to $N \times 10^{-6}$. The change orange to nearly colourless (salt formed with hydrochloric acid) occurs on increasing the concentration of hydrogen ions from $N \times 10^{-2}$ to $N \times 10^{-1}$.

2 : 3 : 6-*Trinitro-4-acetylaminophenol.*—The absorption spectra of this compound in alcoholic solutions containing excess of hydrogen chloride, sodium acetate, and sodium hydroxide respectively have been previously recorded (T., 1910, **97**, 456). The first solution evidently contains the non-ionised compound, the second a non-hydrolysed but easily ionisable monosodium salt, and the third probably a disodium salt easily hydrolysed on dilution. The constitutions of these substances are probably

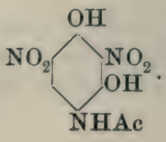




and



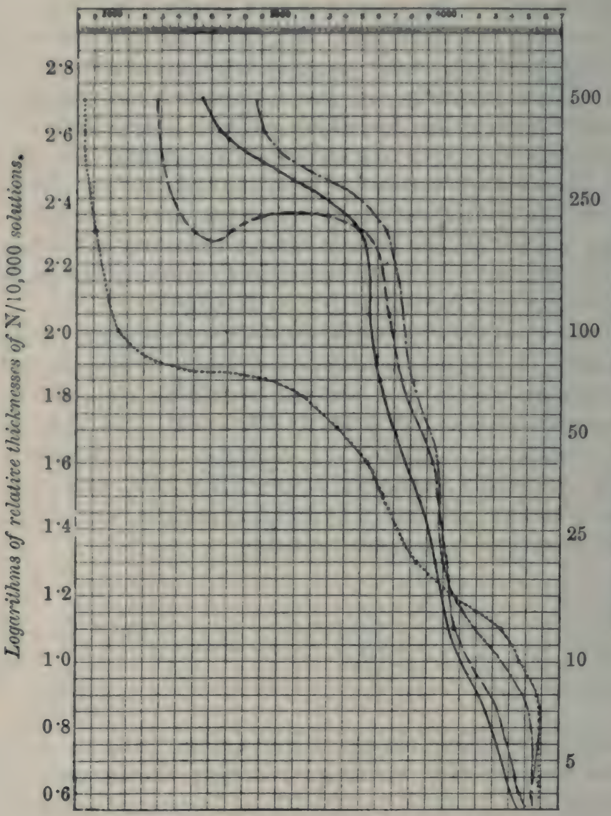
respectively. The colour change corresponding with the formation of the monosodium salt occurs on reducing the concentration of the hydrogen ions from $N$ to $N \times 10^{-1}$; the second colour change with formation of dibasic salt between $N \times 10^{-11}$ and $N \times 10^{-12}$. At the time of the former publication no proof was given that the second colour change was not accompanied by removal of the "mobile" nitro-group (3) with the formation of a salt of a dinitroacetylaminoresorcinol:



That this is not the case was shown by the following experiment: Trinitroacetylaminophenol was dissolved in sufficiently concentrated alkali to give the purple solution; this was then acidified and extracted with ether. The solid residue left on evaporating the solvent resembled the original phenol in appearance, and in solution gave the colour changes for the same alterations in concentration of hydrogen ions.

FIG. 3.

*Scale of oscillation frequencies.*



——— 2 : 3 : 6-*Trinitroacetylaminoanisole* (M) *in alcohol.*

……… ,, ,, ,, (M) *in sodium hydroxide.*

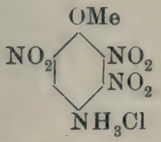
— — — 2 : 6-*Dinitro-4-aminoanisole in alcohol.*

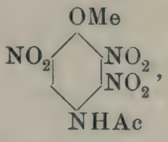
—·—·— ,, ,, ,, *alcoholic hydrochloric acid.*

### *Methyl Ether of* 2:3:6-*Trinitroacetylaminophenol.*

The absorption curve of this compound dissolved in alcohol shows no marked band (Fig. 3), but when an excess of sodium hydroxide is added to the alcoholic solution so that the concentration of hydrogen ions is reduced from $N \times 10^{-9}$ to $N \times 10^{-10}$ a marked colour change, presumably attended by salt formation, is observed (Fig. 3). This change is not accompanied by hydrolysis, as was proved by adding alkali to an alcoholic solution until the deep colour was produced, acidifying the liquid, and recovering the substance thus precipitated. The latter, after being washed and dried, melted at the same temperature as the original material, and, mixed with it, did not depress its melting point.

Curves 3 and 4 of the same figure give the absorption spectra of dinitroanisidine in alcoholic solution and in alcohol to which hydrochloric acid has been added. In the first of these a not very persistent band will be noticed with its head at an oscillation frequency of about 2600, so that addition of hydrochloric acid appears to inhibit the bathochromic effect of the amino-group, and the curve of absorption closely resembles that of the corresponding trinitroacetylaminoanisole. This result is quite in agreement with the constitutions:





the effect of the amino-groups being inhibited in one case by salt-formation, in the other by acylation; the third nitro-group might be expected to have no very profound influence.

### *Methyl Ether of Reverdin's* 2:3:5-*Trinitro*-p-*aminophenol and of the Corresponding Trinitroacetylaminophenol.*

The absorption curves of these two substances in alcoholic solution are shown in Fig. 4. The marked selective absorption of the non-acetylated compound is very noticeable; that of the acetyl derivative, whilst differing from the curve of the isomeric compound, is not altogether dissimilar. In the latter case a deeper colour is produced on addition of alkali, this change being brought about in much the same way, both isomeric acetylamino-compounds showing the change when the hydrogen ion concentration is reduced from $N \times 10^{-9}$ to $N \times 10^{-10}$.

The deep colour and strong selective absorption of the non-acetylated compound are suggestive of its having the constitution of an internal salt:

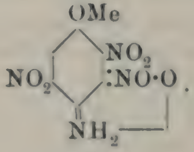
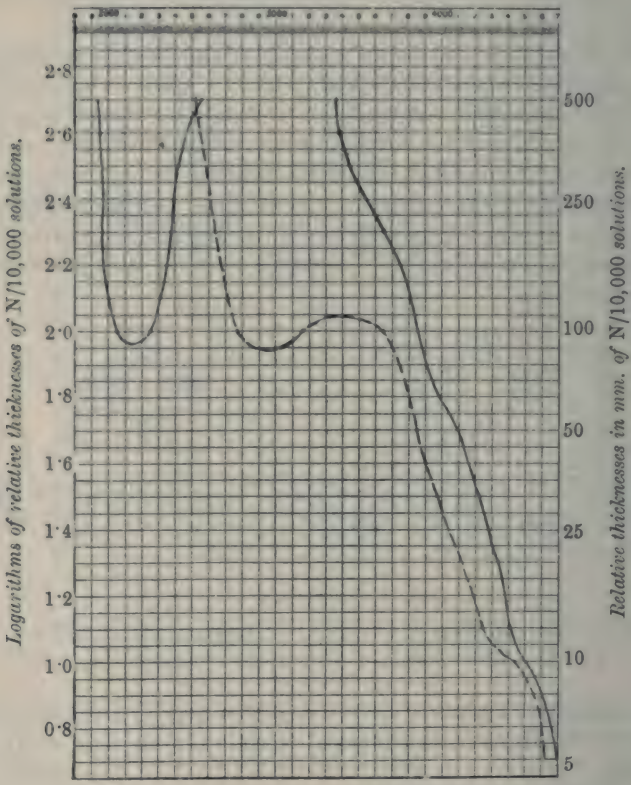


FIG. 4.

*Scale of oscillation frequencies.*



——— 2 : 3 : 5-*Trinitroaminoanisole* (R) *in alcohol.*
— — — 2 : 3 : 5-*Trinitroacetylaminoanisole* (R) *in alcohol.*

In favour of this formula it may be pointed out that the amino-group, being between two ortho-nitro-groups, is in an exceptionally favourable position for the formation of such an internal salt.

We desire in conclusion to express our thanks to M. Reverdin, who has kindly supplied us with the specimens of his compounds referred to in the paper, to Miss R. M. Johnson, who took the photographs of the absorption spectra and plotted the accompanying curves, and to Mr. Wm. F. Hollely, who has rendered valuable assistance in the preparation of all the substances other than those prepared by M. Reverdin.

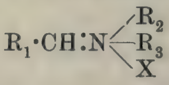
FINSBURY TECHNICAL COLLEGE. EAST LONDON COLLEGE.

## XCI.—*The Carbinol–Ammonium Base Isomerism in Connexion with Azomethine Bases. Part I. Derivatives of Cinnamylidene-*p*-toluidine.*

By CHARLES KENNETH TINKLER.

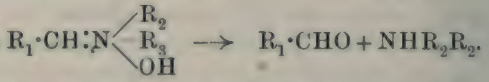
ALTHOUGH in a large number of cases the carbinol-ammonium base isomerism has been investigated in connexion with cyclic bases, only a very limited amount of work has been done in connexion with this isomerism amongst azomethines or Schiff's bases.

During the last ten years this isomerism, as met with in cyclic bases, has been investigated by the author by means of ultra-violet spectroscopy, and following the first paper published on this subject in conjunction with Drs. Dobbie and Lauder on the constitution of cotarnine (T., 1903, **83**, 598), a number of papers in this connexion have been published by the author in conjunction with Dr. Dobbie and independently (T., 1904, **85**, 1007; 1905, **87**, 271; 1906, **89**, 856; 1911, **99**, 1340; 1912, **101**, 1245). The view that cyclic pseudo-bases are more correctly represented as open-chain aldehydes than as closed-chain carbinols is still apparently held by some chemists, and although much of the chemical evidence and the whole of the evidence obtained from the spectroscopic investigation points to the carbinol structure for these bases, it seemed highly desirable to attempt the preparation of a stable quaternary salt of an azomethine compound, with a view to the investigation of alkalis and potassium cyanide on it. If the action of an alkali on such a compound having the linking:



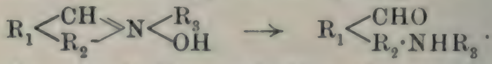
$$R_1\cdot CH{:}N{\lessgtr}\begin{matrix}R_2\\R_3\\X\end{matrix}$$

gives rise to an aldehyde, produced by rearrangement of the quaternary ammonium hydroxide, then in the case of an azomethine compound such action of alkali should obviously lead to the disruption of the molecule, with the production of free aldehyde and secondary amine:



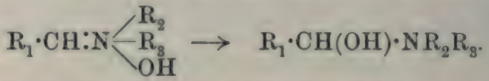
$$R_1\cdot CH\colon N\left\langle\begin{matrix}R_2\\R_3\\OH\end{matrix}\right. \longrightarrow R_1\cdot CHO + NHR_2R_2.$$

In the case, however, of a cyclic base where $R_1$ and $R_2$ are united, even if an aldehyde is produced, it does not lead to the splitting up of the molecule, but simply to the opening of a ring:



$$R_1\left\langle\begin{matrix}CH\\R_2\end{matrix}\right\rangle N\left\langle\begin{matrix}R_3\\OH\end{matrix}\right. \longrightarrow R_1\left\langle\begin{matrix}CHO\\R_2\cdot NHR_3\end{matrix}\right. .$$

On the other hand, the production of a carbinol from the quaternary ammonium hydroxide of an azomethine compound will not lead to the disruption of the molecule, but give rise to a substance derived from a reduced azomethine base:

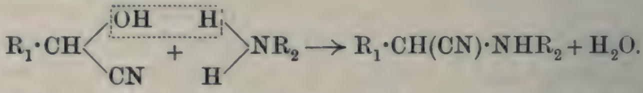


$$R_1\cdot CH\colon N\left\langle\begin{matrix}R_2\\R_3\\OH\end{matrix}\right. \longrightarrow R_1\cdot CH(OH)\cdot NR_2R_3.$$

It is well known that in a large number of cases the action of potassium cyanide on the quaternary salts of cyclic bases gives rise to a pseudo-cyanide instead of a true salt, from which it appears that the cyanogen group, like the hydroxyl group, is mobile. In all cases, these pseudo-cyanides appear to be derived from the carbinol form of the base by substitution of the cyanogen for the hydroxyl radicle. It has frequently been shown that the addition of hydrocyanic acid to an azomethine compound takes place as follows:

$$R_1\cdot CH\colon NR_2 + HCN \longrightarrow R_1\cdot CH(CN)\cdot NHR_2;$$

that is, a pseudo-cyanide, or nitrile, is produced (von Miller and Plöchl, *Ber.*, 1892, **25**, 2056; 1898, **31**, 2699; Morgan, T., 1900, **77**, 1210). The same compounds can also be prepared by the action of the cyanohydrin of the aldehyde on the amine from which the azomethine is produced:



$$R_1\cdot CH\left\langle\begin{matrix}\boxed{OH\qquad H}\\ + \\ CN\qquad H\end{matrix}\right\rangle NR_2 \longrightarrow R_1\cdot CH(CN)\cdot NHR_2 + H_2O.$$

From this method of preparation, the constitution of these substances is apparent.

On account of the ease with which the linking $\colon C\colon N\cdot$ of an azomethine is converted to $\vdots C\cdot N\colon$ by the action of hydrogen cyanide, by reduction (O. Fischer, *Ber.*, 1886, **19**, 748), or by the action of Grignard reagents (Busch, *Ber.*, 1904, **37**, 2691), it appeared likely that it would be possible to obtain evidence of the production of a carbinol and a pseudo-cyanide, by the action of a soluble base and cyanide respectively on the quaternary salt of an azomethine, if such salt could be prepared.

The spectroscopic method of investigation appeared to be especially suitable for this purpose, since the spectra of the nitrile and true salts, and hence of the carbinol and ammonium forms of the base, derived from the azomethine, should be quite distinct.

Attempts to prepare alkyl iodides of Schiff's bases were made by Hantzsch and Schwab (*Ber.*, 1901, **34**, 837), in order that the action of alkalis on these substances might be investigated. The substances which were prepared were, however, extremely unstable. Thus, the most stable compound prepared by these investigators, *p*-tolylbenzylidene-ethylammonium iodide, is decomposed on solution and in moist air. With alkali the following reaction took place:

$$\mathrm{CHPh\vdots NEtI{\cdot}C_6H_4Me + KOH \longrightarrow CHPh\vdots N{\cdot}C_6H_4Me + C_2H_5{\cdot}OH + KI.}$$

With water the substance is further decomposed, owing to the liberation of hydriodic acid, which causes the hydrolysis of the azomethine:

$$\mathrm{CHPh\vdots NEtI{\cdot}C_6H_4Me + 2H_2O \longrightarrow C_6H_5{\cdot}CHO + C_6H_4Me{\cdot}NH_2 + C_2H_5{\cdot}OH + HI.}$$

Hantzsch and Schwab pointed out that, contrary to expectation, no monoethyl-*p*-toluidine was produced. Thus no indication was obtained by these investigators of the production of a pseudo-base of the carbinol form, or even of the secondary amine which would be obtained if the free quaternary ammonium base were converted into free aldehyde and amine. Similar results were obtained by Hantzsch and Schwab in connexion with the somewhat less stable benzylidene-*p*-toluidine methiodide.

In the present investigation the methiodide and ethiodide of benzylidene-*p*-toluidine described by Hantzsch and Schwab (*loc. cit.*) were prepared, and the former was investigated spectroscopically. A solution of this methiodide in alcohol shows comparatively little absorption, owing to the decomposition of the substance, and practically no change in spectra is produced on the addition of soluble base to such a solution. By dissolving the methiodide in an alcoholic solution of sodium hydroxide, the spectra are of the same type as those of the parent base, benzylidene-*p*-toluidine. These results are what would be expected in view of the observations of Hantzsch and Schwab on the decomposition of these quaternary salts.

In the choice of a suitable azomethine base for the attempted preparation of more stable quaternary salts, it appeared desirable to make use of a base having alkyl instead of aryl radicles attached to the nitrogen atom, in order to increase the basicity of the substance, but in view of the fact that such bases are highly polymerised, this idea was abandoned.

Cinnamylideneaniline * is described as a Schiff's base which gives rise to a fairly stable hydrochloride and sulphate, which is unusual for these azomethine compounds (Doebner and Miller, *Ber.*, 1883, **16**, 1665).

In view of the fact that Hantzsch and Schwab found that the alkyl iodides of benzylidene-*p*-toluidine were more stable than the corresponding aniline compounds, it was decided to prepare cinnamylidene-*p*-toluidine, and to investigate the action of alkyl esters on this base, with the view of the application of such additive compounds to the investigation of the carbinol-ammonium base isomerism.

By the action of methyl iodide on cinnamylidene-*p*-toluidine dissolved in a mixture of ether and benzene, a crystalline mass is produced, which consists apparently of a mixture of the methiodide with a colourless substance. On attempting to crystallise the methiodide from alcohol, the crystalline substance produced is found to be the *hydriodide* of the base, and not the methiodide. This is proved by analysis, and by the identity of the hydriodide prepared by this method and the salt prepared from the base and hydriodic acid. The methiodide of cinnamylidene-*p*-toluidine is therefore decomposed by alcohol, like the methiodides described by Hantzsch and Schwab (*loc. cit.*), but in the case of the present substance the hydriodide is a stable substance, and so separates from the solution. The spectra of an alcoholic solution of the methiodide both before and after recrystallisation differ considerably from those of the parent base, but are in agreement with those of the other salts described later. On the addition of either sodium hydroxide or potassium cyanide to the alcoholic solution of the crude methiodide, the spectra are practically identical with those of the free base, and are quite distinct from those of *a*-*p*-toluidino-γ-phenyl*iso*crotononitrile, $\mathrm{CHPh{:}CH{\cdot}CH(CN){\cdot}NH{\cdot}C_6H_4Me}$ (Figs. I and II). If by the addition of soluble base or cyanide to the solution of this quaternary salt, assuming that in a freshly-made cold solution some of the substance is present as quaternary salt, a carbinol or pseudo-cyanide had been produced, the spectra of the solutions should have been in close agreement with those of the above nitrile. It appears therefore that no such carbinol or pseudo-cyanide is produced, but that the quaternary salt is decomposed with liberation of the parent base.

The action of methyl sulphate on cinnamylidene-*p*-toluidine was next investigated. A crystalline substance is produced by the action of methyl sulphate on a solution of the base in a mixture of ether and benzene. After crystallisation from alcohol, however, this substance is found to be cinnamylidene-*p*-toluidine hydrogen methosulphate. As in the case of the methiodide, this is proved by analysis and by the identity of the substance with cinnamylidene-*p*-toluidine hydrogen methosulphate prepared from the base and methylsulphuric acid. The spectra of an alcoholic solution of the substance resulting from the interaction of the base and methyl sulphate both before and after recrystallisation agree with those of the other salts.

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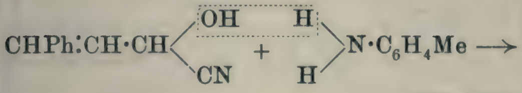
* This substance is wrongly described in the literature as "Zimmtanilid."

On the addition of a soluble base or cyanide, no indication of the formation of either a pseudo-base or cyanide is obtained, the spectra in both cases being identical with those of the parent base.

The crude methiodide and methosulphate are both decomposed by water, giving, on boiling, free aldehyde, amine, and acid like the quaternary iodides of benzylidene-*p*-toluidine described by Hantzsch and Schwab.

A possible explanation of the remarkable decomposition of these quaternary substances by alkali and water is put forward later in this paper.

The *α*-p-*toluidino-γ-phenyl*iso*crotononitrile* referred to above was prepared in the usual manner by the action of cinnamaldehydecyanohydrin on *p*-toluidine:



$$\mathrm{CHPh{:}CH{\cdot}CH}\left\langle\begin{matrix}\boxed{\mathrm{OH}\quad\quad\mathrm{H}}\\ \mathrm{CN}\quad+\quad\mathrm{H}\end{matrix}\right\rangle\mathrm{N{\cdot}C_6H_4Me}\longrightarrow$$

$$\mathrm{CHPh{:}CH{\cdot}CH(CN){\cdot}NH{\cdot}C_6H_4Me}.$$

This substance is of interest from the fact that it gives different spectra in ethereal and alcoholic solution, and also that the alcoholic solution does not follow Beer's law.

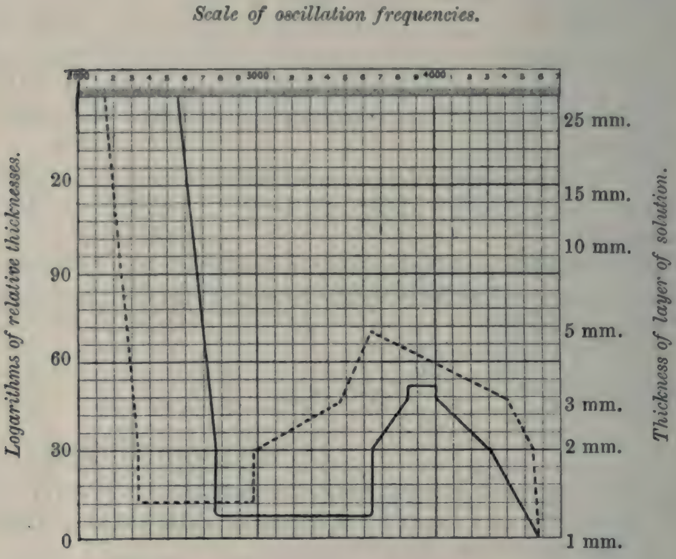
In the case of the pseudo-cyanides of cyclic bases, it has previously been pointed out by the author that these substances are partly converted by alcohol into true cyanides. The spectra of dilute alcoholic solutions of this nitrile show that the solution contains a substance of constitution analogous to that of the free azomethine base, and it is thus obvious that if a cyanide is formed it is not of similar constitution to the ordinary salts of cinnamylidene-*p*-toluidine, for, as previously mentioned, the spectra of these salts differ widely from those of the parent base. It is possible that in this case the pseudo-cyanide simply loses hydrogen cyanide with the formation of azomethine base, as is certainly the case when a dilute alcoholic solution of the substance is heated:

$$\mathrm{CHPh{:}CH{\cdot}CH(CN){\cdot}NH{\cdot}C_6H_4Me} \longrightarrow$$
$$\mathrm{CHPh{:}CH{\cdot}CH{:}N{\cdot}C_6H_4Me + HCN}.$$

The reverse reaction between hydrogen cyanide and the azomethine base has also been investigated. By treating cinnamylidene-*p*-toluidine dissolved in a mixture of ether and benzene with anhydrous gaseous hydrogen cyanide, α-*p*-toluidino-γ-phenyl*iso*crotononitrile separates out. The identity of this substance with the nitrile prepared from cinnamaldehydecyanohydrin and *p*-toluidine was established by its melting point, analysis, and absorption spectra.

In addition to the methiodide, hydriodide, methosulphate, and hydrogen methosulphate, the additive compounds of cinnamylidene-*p*-toluidine with hydrochloric, hydrobromic, sulphuric, and nitric acids were prepared and analysed. These salts were prepared for use partly in connexion with the present investigation, and also for investigation in connexion with Hantzsch's theory of "chromoisomerism" (*Ber.*, 1911, **44**, 1783, etc.). It was pointed out by the author (T., 1909, **95**, 921) that the salts which show this phenomenon contain an unreduced pyridine, etc., nucleus, and since it is not shown by such substances as tetrapropylammonium iodide, which do not contain the nitrogen atom in a ring, it appeared of

Fig. 1.



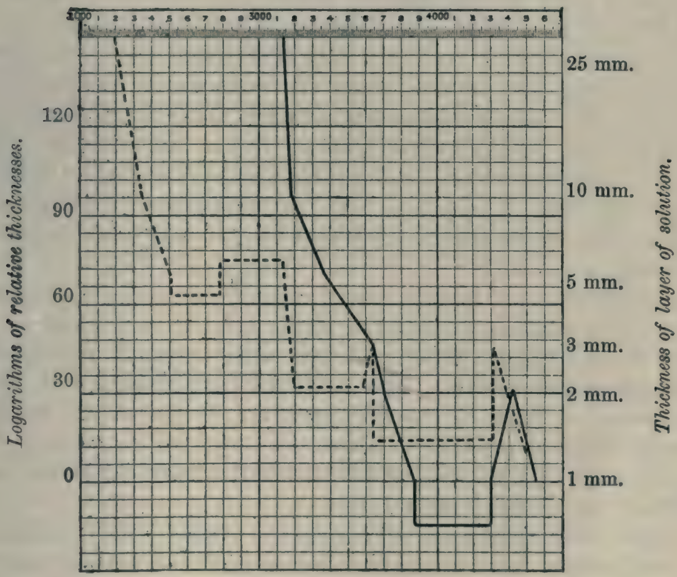
——— *Cinnamylidene*-p-*toluidine in alcohol.*
1 *Mg.-mol. in* 1000 *c.c.*
- - - - - *Cinnamylidene*-p-*toluidine hydrochloride in alcohol.*
1 *Mg.-mol. in* 1000 *c.c.*

interest in this connexion to investigate the salts of azomethines, which should contain the linking ⁚C⁚N·.

The above-mentioned salts of cinnamylidene-*p*-toluidine were prepared by heating the base on the water-bath with a dilute solution of the acid. As a general rule, by such treatment an azomethine base is decomposed into free aldehyde and amine, but although a certain amount of decomposition appears to take place with cinnamylidene-*p*-toluidine in such circumstances, the crystalline salts separate from the filtrate.

FIG. 2.

*Scale of oscillation frequencies.*



——— α-p-*Toluidino-γ-phenyl*iso*crotononitrile in ether.*
1 *Mg.-mol. in* 1000 *c.c.*
- - - - - *Cinnamylidene-*p*-toluidine hydrochloride in alcohol*
*after twenty-four hours.*
1-*Mg.-mol. in* 1000 *c.c.*

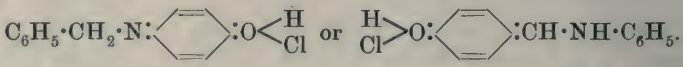
The salts in all cases are produced by the combination of one molecule of the base with one molecule of acid, so that in the case of the sulphate it is the acid salt that is produced. The halogen salts were also prepared by passing the halogen hydride into a benzene solution of the base. All these salts are considerably darker in colour than the parent base, and they also differ widely amongst themselves in their colour intensity. The bearing of these salts on the phenomenon of chromoisomerism will be dealt with in a later communication. In connexion with the present investigation, however, the following results may be mentioned.

The spectra of an alcoholic solution of the hydrochloride differ considerably from those of the parent base (Fig. 1). On the addition of aqueous hydrochloric acid to an alcoholic solution of the free base, the spectra obtained are quite distinct from those of a freshly-made alcoholic solution of the hydrochloride, but are similar to those of an alcoholic solution of this substance which has been prepared some time (Fig. 2). This is explained on the assumption that the addition of aqueous hydrochloric acid to the alcoholic solution of the base causes partial hydrolysis, and this view receives support from the fact that the longer a solution of the hydrochloride has been made the more nearly do the spectra approach those of the colourless solution made by the prolonged action of water on the hydrochloride. In the last case the solution contains cinnamaldehyde and *p*-toluidine hydrochloride, since the spectra of such a solution are in agreement with those of cinnamaldehyde, *p*-toluidine hydrochloride at this dilution showing no absorption.

On the addition of soluble base or cyanide to an alcoholic solution of the hydrochloride, the spectra of the solution are identical with those of the parent base, and not with those of *a*-*p*-toluidino-γ-phenyl*iso*crotononitrile. This result in both cases is what would be expected in view of the decomposition of the nitrile in dilute alcoholic solution referred to above.

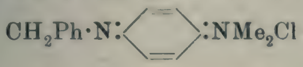
The spectra of a chloroform solution of the hydrochloride undergo no change on keeping the solution.

As previously mentioned, all the salts of cinnamylidene-*p*-toluidine are considerably more strongly coloured than the parent base, and in this respect they resemble the hydrochlorides of azomethine bases described by F. G. Pope and Fleming (T., 1908, **93**, 1914) and by F. J. Moore and his co-workers (*J. Amer. Chem. Soc.*, 1908, **30**, 394, 1001; 1910, **32**, 382). These investigators assign a quinonoid structure to certain coloured salts of azomethine bases. Thus Pope and Fleming represent the hydrochlorides of hydroxyazomethine bases as either:

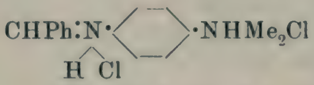


Moore and his co-workers point out that three explanations are possible of the differences in colour of the red monohydrochloride of the Schiff's base benzylidene-*p*-aminodimethylaniline on the one hand, and the yellow parent base and dihydrochloride on the other. The explanation favoured by Moore is that which assigns a quinonoid constitution to the more strongly coloured salts, and some evidence in support of this theory was obtained by him from the fact that the corresponding meta-substituted compounds do not, as a rule, give rise to red salts.

The hydrochlorides of benzylidene-*p*-aminodimethylaniline are represented by Moore thus:

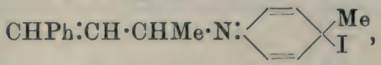


Red monohydrochloride, quinonoid.



Yellow dihydrochloride, benzenoid.

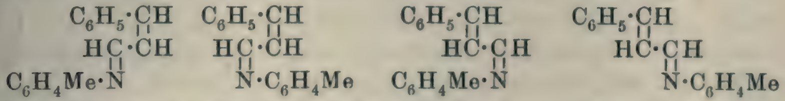
A similar explanation of the coloured salts of substituted azo-compounds was put forward by Hewitt and his co-workers (T., 1909, **95**, 1292, 1393, etc.). The possibility of a quinonoid constitution for the salts derived from cinnamylidene-*p*-toluidine must therefore be taken into account. Such a constitution would not only explain the differences in colour between the salts and the parent base, but would also explain why no indication of a pseudo-base is obtained when cinnamylidene-*p*-toluidine methiodide is treated with alkali. Thus, if this substance is represented by the formula:



it would not be expected that a substance of the formula $CHPh:CH\cdot CH(OH)\cdot NMe\cdot C_6H_4Me$ would be obtained from it by the action of alkali.

The differences in colour shown by a number of Schiff's bases under varying conditions have recently been investigated by Senier and his co-workers (T., 1909, **95**, 1943; 1911, **99**, 2081; 1912, **101**, 1950). These investigators are of opinion that such phenomena may be explained by the molecular aggregation of the bases in the solid state.

It will be noticed that cinnamylidene-*p*-toluidine is capable of existence in four stereoisomeric modifications:



$$\begin{array}{rl} C_6H_5\cdot & CH \\ & \| \\ H & C\cdot CH \\ & \| \\ C_6H_4Me\cdot & N \end{array} \qquad \begin{array}{rl} C_6H_5\cdot & CH \\ & \| \\ H & C\cdot CH \\ & \| \\ & N\cdot C_6H_4Me \end{array} \qquad \begin{array}{rl} C_6H_5\cdot & CH \\ & \| \\ & HC\cdot CH \\ & \qquad\| \\ C_6H_4Me\cdot & N \end{array} \qquad \begin{array}{rl} C_6H_5\cdot & CH \\ & \| \\ & HC\cdot CH \\ & \qquad\| \\ & \qquad N\cdot C_6H_4Me \end{array}$$

and it is quite possible that the salts are derived from a different isomeride than is represented by the parent base, although, as a rule, the difference between the absorption spectra of *cis*- and *trans*-isomerides is only slight.

## EXPERIMENTAL.

### *Cinnamylidene*-p-*toluidine*, $C_6H_5 \cdot CH\!:\!CH \cdot CH\!:\!N \cdot C_6H_4Me$.

This substance is readily prepared by gently warming a mixture of molecular quantities of cinnamaldehyde and *p*-toluidine. The mass solidifies on cooling, and after drying on a porous plate and crystallisation from alcohol, the base is obtained in pale yellow plates, which melt at 83°. The base is readily soluble in alcohol or benzene, less so in ether or light petroleum:

0·3153 gave 17·6 c.c. $N_2$ (moist) at 16° and 759 mm. N = 6·49.

$C_{16}H_{15}N$ requires N = 6·34 per cent.

### *Action of Methyl Iodide on Cinnamylidene*-p-*toluidine.*

The base dissolved in ether containing a little benzene is treated with a slight excess of methyl iodide, and the mixture allowed to remain in the ice-chest for several days. A crystalline mass separates, which, under the microscope, is seen to be a mixture of a coloured and colourless substance. On recrystallisation from alcohol, a reddish-yellow substance is produced, which melts at 183°:

I. 0·1352 gave 0·0901 AgI. I = 36·02.

II. 0·1040 required 14·78 c.c. *N*/50-$AgNO_3$. I = 36·07.

$C_{16}H_{15}N,CH_3I$ requires I = 34·96 per cent.

$C_{16}H_{15}N,HI$ „ I = 36·36 „

The hydriodide prepared from the base and hydriodic acid, when mixed with the recrystallised methiodide, produces no lowering of the melting point.

### *Action of Methyl Sulphate on Cinnamylidene*-p-*toluidine.*

The base dissolved in a mixture of ether and benzene is treated with a slight excess of methyl sulphate. After remaining some days at the ordinary temperature, the whole mass becomes practically solid. The substance, after washing with ether, may be crystallised from alcohol. Under the microscope these crystals are seen to be fine, long, rectangular prisms.

The substance, after recrystallisation, is reddish-yellow, and melts and decomposes at 205°:

0·2212 gave 8·1 c.c. $N_2$ (moist) at 16° and 761·5 mm. N = 4·26.

0·1634 „ 0·1159 $BaSO_4$. S = 9·74.

$C_{16}H_{15}N,MeHSO_4$ requires N = 4·22; S = 9·62 per cent.

The hydrogen methosulphate of cinnamylidene-*p*-toluidine prepared from the base and methylsulphuric acid is identical in all respects with this substance.

### α-p-*Toluidino-γ-phenyl*iso*crotononitrile*, $C_6H_5{\cdot}CH{:}CH{\cdot}CH(CN){\cdot}NH{\cdot}C_6H_4Me$.

This substance was prepared by the condensation of cinnamaldehydecyanohydrin with *p*-toluidine. After heating the substances in molecular proportions in alcoholic solution for several hours on the water-bath, the nitrile separates on cooling. It is crystallised from light petroleum, in which it is sparingly soluble, and is obtained in colourless leaflets, melting at 119°.

This nitrile may also be prepared by the action of anhydrous gaseous hydrogen cyanide on a solution of cinnamylidene-*p*-toluidine in ether containing a little benzene. After the gas has been passed into the solution for some time, colourless crystals of the nitrile separate, and after washing with ether the substance has the same melting point (119°) as the nitrile prepared by the former method:

0·1414 * gave 14·3 c.c. $N_2$ (moist) at 16° and 742·1 mm. N = 11·46.
0·1642 † „ 15·9 c.c. $N_2$ „ „ 10° „ 742·3 mm. N = 11·41.
$C_{17}H_{16}N_2$ requires N = 11·29 per cent.

### *Additive Compounds of Cinnamylidene*-p-*toluidine with Acids.*

### *Cinnamylidene*-p-*toluidine Hydrochloride*, $C_{16}H_{15}N,HCl$.

This substance may be prepared by heating the base on the water-bath with dilute hydrochloric acid. After filtering, the salt separates on cooling in fine, reddish-yellow needles. After recrystallisation from alcohol, the substance has a deep yellow colour, and melts at 188—190°. It is sparingly soluble in alcohol or chloroform, and is decomposed by boiling water. The salt may also be prepared by passing gaseous hydrogen chloride into a benzene solution of the base:

0·2997 gave 0·1674 AgCl. Cl = 13·81.
10 c.c. of an *N*/100-solution required 5·0 c.c. 0·999 *N*/50-$AgNO_3$. Cl = 13·76.
$C_{16}H_{15}N,HCl$ requires Cl = 13·77 per cent.

After heating the alcoholic solution of this salt for twenty hours at 25°, the volume of silver nitrate solution required was unchanged.

The *hydrobromide*, like the hydrochloride, is prepared by warming the base with dilute hydrobromic acid and crystallisation from alcohol, or by passing gaseous hydrogen bromide into a benzene solution of the base.

The substance is darker in colour than the hydrochloride, and melts at 206°.

The percentage of acid in this and the salts described below may be estimated by warming with excess of standard sodium hydroxide solution and a little alcohol and titration of the excess of alkali:

---

* Prepared by first method. † Prepared by second method.

0·1295 required 7·9 c.c. 1·083 *N*/20-NaOH. HBr = 26·73.

$C_{16}H_{15}N,HBr$ requires HBr = 26·79 per cent.

The *hydriodide* can be prepared by either of the methods employed in the preceding cases. It may be crystallised from alcohol, and has a reddish-yellow colour, which is deeper than that of the bromide; it melts at 183°:

0·1302 required 3·45 c.c. 1·063 *N*/10-NaOH. HI = 36·35.

$C_{16}H_{15}N,HI$ requires HI = 36·65 per cent.

The *hydrogen sulphate*, $C_{16}H_{15}N,H_2SO_4$, is obtained in minute crystals by warming the base with dilute sulphuric acid. After recrystallisation from alcohol, the substance melts at 193°:

0·0682 required 7·65 c.c. 1·083 *N*/20-NaOH. $H_2SO_4$ = 29·8.

$C_{16}H_{15}N,H_2SO_4$ requires $H_2SO_4$ = 30·73 per cent.

This salt is darker in colour than any of the others.

The *hydrogen methosulphate*, $C_{16}H_{15}N,MeHSO_4$, is prepared by warming the base with an aqueous solution of methylsulphuric acid. After crystallisation from alcohol, the substance melts and decomposes at 205°:

0·1636 gave 6·2 c.c. $N_2$ (moist) at 16·5° and 749·4 mm. N = 4·32.
0·1543 „ 0·1098 $BaSO_4$. S = 9·78.

$C_{16}H_{15}N,MeHSO_4$ requires N = 4·22; S = 9·62 per cent.

The *nitrate*, $C_{16}H_{15}N,HNO_3$, separates from a solution of the base in warm dilute nitric acid. It is much paler in colour than any of the other salts except the hydrochloride:

0·0895 required 2·8 c.c. 1·083 *N*/10-NaOH. $HNO_3$ = 21·85.

$C_{16}H_{15}N,HNO_3$ requires $HNO_3$ = 22·19 per cent.

The *orthophosphate*, *perchlorate*, and *trichloroacetate* can also be prepared by warming the base with a solution of the corresponding acid. The *picrate* is precipitated on mixing benzene solutions of the base and picric acid.

Some of the materials used in this investigation were purchased by means of a grant made by the Research Fund Committee of the Chemical Society, for which the author wishes to express his thanks.

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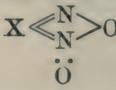
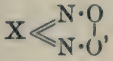
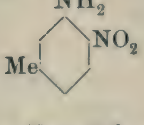
BIRMINGHAM.

# XCII.—*The Constitution of Oxadiazole Oxides (Furazan Oxides or Dioxime Peroxides).*

By Arthur George Green and Frederick Maurice Rowe.

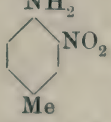
In a former communication (T., 1912, **101**, 2452) we have published a new method of formation of compounds belonging to the class described originally by Noelting and Kohn and by Zincke and Schwarz as "ortho-dinitroso-derivatives," but regarded later by Forster and Fierz (T., 1907, **91**, 1942) as *o*-quinonedioxime peroxides. This reaction consists in the oxidation of *o*-nitroamines with sodium hypochlorite in an alkaline solution. In view of the improbability of a transference of an oxygen atom from the nitro- to the amino-nitrogen, the new method of formation appeared to indicate for these compounds an unsymmetrical structure represented by the formula  $X{<\!\!\!<}\begin{matrix}N\\ \underset{\ddot{O}}{N}\end{matrix}{>}O$, in place of the dioxime-peroxide constitution,  $X{<\!\!\!<}\begin{matrix}N\cdot O\\ \vert\\ N\cdot O\end{matrix}$, advocated by Forster and Fierz. On the other hand, these authors have stated that one and the same "$\beta$-naphthaquinonedioxime peroxide" melting at 127° (identical with Koreff and Ilinki's "1:2-dinitrosonaphthalene" formed by oxidation of $\beta$-naphthaquinonedioxime) is obtained on heating either 2-nitro-1-naphthylazoimide or 1-nitro-2-naphthylazoimide, $NO_2\cdot C_{10}H_6\cdot N_3$, thus indicating a symmetrical structure for the product.

In order to obtain further evidence on the point in question, we have submitted to the sodium hypochlorite oxidation the pair of nitrotoluidines:



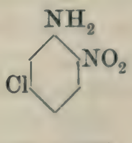
M. p. 109°.

and



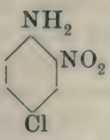
M. p. 114°.

and the pair of chloronitroanilines:



M. p. 125°.

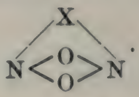
and



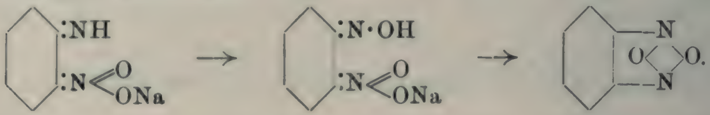
M. p. 116°.

with the object of ascertaining whether isomeric or identical furazan oxides result.

In each case the same oxidation product was obtained from both isomerides, thus confirming Forster and Fierz's observations in the naphthalene series. Symmetrical structure for the furazan oxides is thus definitely established, but in view of the objections already stated to the glyoxime-peroxide formula it appears more probable that the compounds in question have the constitution



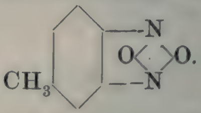
This formula would represent their formation from the nitroamines without requiring the transference of an oxygen atom from the nitro-group, and it also stands in better accord with their chemical properties. The reaction may be regarded as taking place through the intermediate formation of quinonoid compounds, according to the scheme:



## Experimental.

### 5-*Methylbenzisooxadiazole Oxide.*

(*Tolufurazan Oxide, Tolufuroxan,* "*Dinitrosotoluene,*" *or* "o-*Toluquinonedioxime Peroxide*"),



The preparation of this compound from *m*-nitro-*o*-toluidine (m. p. 114°) by oxidation with sodium hypochlorite has already been described in our former paper (*loc. cit.*).

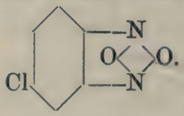
In order to subject *p*-nitro-*m*-toluidine to the same treatment, this base was prepared according to Städel and Kolb's method (*Annalen*, 1890, **259**, 208). Pure *m*-cresol was nitrated in glacial acetic acid solution below 0°, and the portion of the product volatile with steam, nitro-*m*-cresol (m. p. 56°), was converted into the potassium salt and then through the silver salt into the ethyl ether. The nitro-*m*-tolyl ethyl ether obtained melted at 50—51°. To convert this into the nitrotoluidine it was dissolved in a little alcohol and heated with aqueous ammonia in a sealed tube for twelve hours at 200° (heating with aqueous ammonia at 140—150° as prescribed by Städel and Kolb gave only a small yield). When crystallised from dilute alcohol the *p*-nitro-*m*-toluidine formed yellow plates melting at 109°.

The oxidation with sodium hypochlorite was effected in alkaline alcoholic solution in a similar manner to that employed for the isomeric base. The product formed white needles melting at 97° (Found, N = 18·69), which proved to be completely identical with that from *m*-nitro-*p*-toluidine (Found, N = 18·81. Calc., N = 18·66 per cent.). It had the same crystalline form, and melted at exactly the same temperature. Mixtures of the two products also had the same melting point.

On reduction with alkaline hydroxylamine the tolufurazan oxide from *p*-nitro-*m*-toluidine gave 3 : 4-toluquinonedioxime (m. p. 128°: Found, N = 18·55. Calc., N = 18·43 per cent.) From this the methylbenz*iso*oxadiazole (tolufurazan) melting at 37° was obtained by distilling the alkaline solution in a current of steam (Found, N = 20·91. Calc., N = 20·89 per cent.). Both compounds were completely identical with those obtained previously from *m*-nitro-*p*-toluidine.

### *Chlorobenz*isoo*xadiazole oxide.*

(*Chlorobenzfurazan Oxide, Chlorobenzfuroxan*),



(1) *Preparation from* m-*Chloro*-o-*nitroaniline*.—This base was obtained by Beilstein and Kurbatov's method (*Annalen*, 1876, **182**, 102) by nitration of *m*-chloroacetanilide, saponification of the product and separation from the chloro-*p*-nitroaniline by distillation in a current of steam. When crystallised from benzene it was obtained in golden crystals melting at 125°. The oxidation with sodium hypochlorite was effected in alkaline alcoholic solution in the usual way. The product, which separates on keeping, was crystallised from alcohol, and found to melt at 48°:

0·1809 gave 25·8 c.c. $N_2$ at 17° and 747 mm. N = 16·63.
0·1392 „ 0·1167 AgCl. Cl = 20·74.

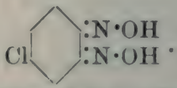
$C_6H_3O_2N_2Cl$ requires N = 16·43; Cl = 20·83 per cent.

(2) *Preparation from* p-*Chloro*-o-*nitroaniline*.—This base was obtained in theoretical yield by heating 2 : 5-dichloronitrobenzene (m. p. 55°), dissolved in sufficient alcohol, with aqueous ammonia under pressure at 190° for eight hours. The product melted at 116·5°. The oxidation with alkaline sodium hypochlorite can be conducted in alcoholic or in aqueous solution. In the latter case the base is dissolved in hot water, rendered alkaline with sodium

hydroxide, and sodium hypochlorite added until the deep orange-red colour disappears. The product which separates on cooling is crystallised from alcohol:

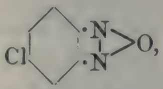
0·1053 gave 14·3 c.c. $N_2$ at 14° and 758 mm. N = 16·46.
0·1697 „ 0·1418 AgCl. Cl = 20·66.
$C_6H_3O_2N_2Cl$ requires N = 16·43; Cl = 20·83 per cent.

The products are completely identical in properties. They crystallise from alcohol in large, pale yellow, readily soluble crystals, melting at 48°. A mixture of the two compounds also melted at the same temperature.

*Chloro-o-benzoquinonedioxime,* 

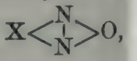
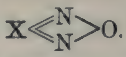
This compound was obtained by reduction of the chlorofurazan oxide prepared from either *m*- or *p*-chloro-*o*-nitroaniline. The reduction was effected in alcoholic solution with alkaline hydroxylamine. The product was a brown, crystalline powder, melting at 128°, having the general properties of *o*-dioximes:

0·0758 * gave 10·7 c.c. $N_2$ at 17° and 746 mm. N = 16·44.
0·0926 † „ 12·7 c.c. $N_2$ „ 14° „ 758 mm. N = 16·40.
0·1018 * „ 0·0845 AgCl. Cl = 20·54.
0·1426 † „ 0·1184 AgCl. Cl = 20·54.
$C_6H_5O_2N_2Cl$ requires N = 16·24; Cl = 20·58 per cent.

*Chlorobenzisooxadiazole* (*Chlorobenzfurazan*),  was

prepared by subjecting to steam distillation an alkaline solution of chlorobenzoquinonedioxime (from *p*-chloro-*o*-nitroaniline). The product forms long, white, silky needles, which melt at 44°. It is readily volatile with steam:

0·0743 gave 11·35 c.c. $N_2$ at 15° and 758 mm. N = 18·20.
0·1202 „ 0·1108 AgCl. Cl = 22·97.
$C_6H_3ON_2Cl$ requires N = 18·12; Cl = 22·98 per cent.

This and other compounds of the same class are probably more correctly represented by formulæ of the benzenoid type,  $\mathrm{X}<\genfrac{}{}{0pt}{}{\mathrm{N}}{\mathrm{N}}>\mathrm{O}$, than by those of the quinonoid type,  $\mathrm{X}\ll\genfrac{}{}{0pt}{}{\mathrm{N}}{\mathrm{N}}>\mathrm{O}$. The absence of colour, and resistance to reduction and oxidation stand in better accord with the former than with the latter view of their structure.

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* From *m*-chloro-*o*-nitroaniline. † From *p*-chloro-*o*-nitroaniline.

Whilst the dioximes are readily converted into the furazan oxides by oxidation in alkaline solution with sodium hypochlorite, the furazans remain unchanged under this treatment. The latter are also strongly basic compounds, forming readily soluble hydrochlorides.

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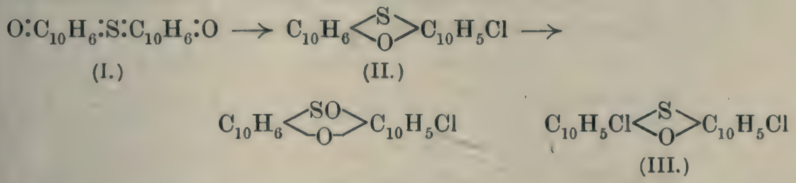
# XCIII.—*Naphthathioxin and* iso*Naphthathioxin.*

By THOMAS JOSEPH NOLAN and SAMUEL SMILES.

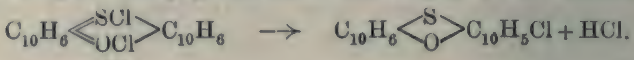
DURING the investigation of the action of acetyl chloride on β-naphthasulphonium-quinone (I), monochloronaphthathioxin (II) was obtained (T., 1912, **101**, 715). This substance was converted into the oxide, and thence, by means of hydrogen chloride, dichloronaphthathioxin (III) was prepared:



$$\underset{\text{(I.)}}{O{:}C_{10}H_6{:}S{:}C_{10}H_6{:}O} \longrightarrow \underset{\text{(II.)}}{C_{10}H_6{<}\substack{S\\O}{>}C_{10}H_5Cl} \longrightarrow$$

$$C_{10}H_6{<}\substack{SO\\O}{>}C_{10}H_5Cl \qquad \underset{\text{(III.)}}{C_{10}H_5Cl{<}\substack{S\\O}{>}C_{10}H_5Cl}$$

Since naphthathioxin had been previously obtained by the dehydration of β-naphthol sulphide, attempts were then made to synthesise the foregoing chloro-compounds by chlorination of the parental substance. Accordingly, the oxide of naphthathioxin (T., 1912, **101**, 714) was converted by the action of hydrogen chloride into the chloro-derivatives. The process yielded a mixture of mono- and di-halogen derivatives, but of these neither was identical with the corresponding substance formed from the quinone. In explanation of this circumstance two alternative hypotheses were available: either that the difference between the two series was solely due to the varying situation of halogen in the naphthalene nuclei, or that the parental thioxin of each was different. The former alternative could only be accepted with some hesitation, for it is in conflict with theoretical views advanced to explain the interaction of the quinone and acetyl chloride (T., 1912, **101**, 711). Without repeating the evidence on which these views were founded, it may be remarked that the conclusion was made that at the penultimate stage the thioxonium chloride is formed (IV), which, losing halogen, finally yields chloro-derivatives of the nucleus:

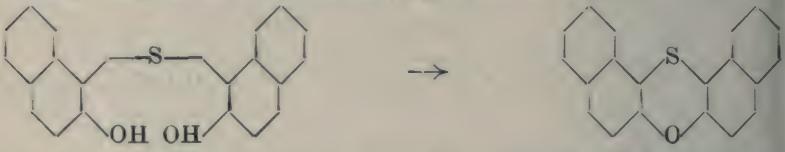


$$C_{10}H_6{<}\overset{SCl}{\underset{OCl}{}}{>}C_{10}H_6 \longrightarrow C_{10}H_6{<}\overset{S}{\underset{O}{}}{>}C_{10}H_5Cl + HCl.$$

(IV.)

This has now been fully confirmed by the isolation of the corresponding thioxonium bromide from the interaction of the quinone and acetyl bromide. In the meantime other experiments (this vol., p. 349, and this paper) have shown that also direct halogenation of the naphthathioxin leads to initial products of this thioxonium type (IV); hence, provided that the parental naphthathioxin is the same in the two series, similar orientation of the halogen in the products of the two methods is to be expected. For these reasons it seemed improbable that the former of the foregoing alternatives is correct, and attention was therefore turned to the possibility of the existence of two isomeric naphthathioxins. Experiment has revealed the existence of these substances.

*Naphthathioxin.*—The naphthathioxin hitherto known is obtained by the dehydration of β-naphthol sulphide (V) with phosphoryl chloride (Mauthner, *Ber.*, 1906, **39**, 1340; Christopher and Smiles, T., 1912, **101**, 713). The constitution (VI) of a thioxin has been already assigned to this substance by Mauthner:



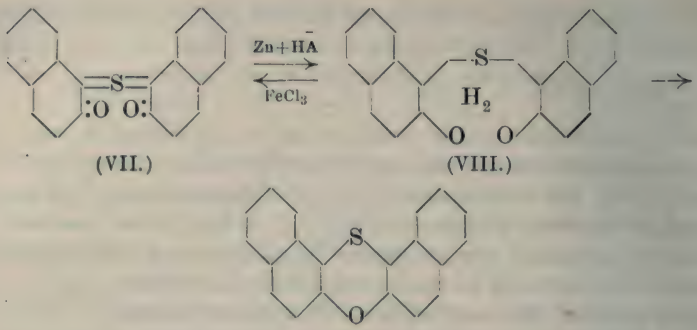
(V.) (VI.)

It need now only be said that this structure clearly follows from the fact that the substance is formed by removal of the elements of water from a dihydroxy-derivative of known constitution (V). Moreover, during the process, the hydroxyl groups disappear, and the product assumes the distinctive character which must be expected of a thioxin from analogy to other similar heterocyclic compounds; thus the substance is readily oxidised by cold concentrated sulphuric acid or by ferric chloride in ethereal solution. It yields an oxide, which is readily transformed by hydrogen chloride or bromide into halogen derivatives of the nucleus. Further oxidation yields a sulphone, whilst with bromine the parent substance furnishes highly coloured additive products, to which the thioxonium structure must be assigned. All these reactions find a strict parallel in the thiazin series.

We have now further examined this substance, and a set of four characteristic derivatives has been prepared for comparison with those obtained from *iso*naphthathioxin. The relations between these substances are summarised in a table given on p. 905, whilst the mode of preparation is described in the experimental part of this paper.

iso*Naphthathioxin.*—The existence of an isomeride of naphthathioxin has been already indicated by experiments (this vol., p. 347) dealing with the interaction of acetic anhydride and the acetyl derivative of *iso*-β-naphthol sulphide. Other more convenient means of preparing the substance by dehydrating *iso*-β-naphthol sulphide are described in the experimental part of this paper. The melting point of this anhydride of *iso*-β-naphthol sulphide lies only some 15° apart from that of the naphthathioxin derived from β-naphthol sulphide; but the lowering in melting point of a mixture of the compounds and the existence of two distinct sets of derivatives shows that the substances are not identical. A summary of these derivatives is given on a subsequent page.

*Constitution.*—The molecular weights of the two substances measured in the same solvent corresponds with the simple formula derived from the sulphides by intramolecular loss of the elements of water. The thioxin structure for this *iso*anhydride is advanced by the following argument. The presence of the thio-arrangement is demonstrated by the successive formation of a sulphoxide and a sulphone when the substance is treated with oxidising agents. Direct evidence showing the oxide grouping cannot be adduced, but the presence of oxygen in this form may be inferred from the fact that hydroxyl or carbonyl cannot be detected by the usual reagents in the parental substance or its derivatives. In further support of the thioxin structure it must be observed that this anhydride of *iso*-β-naphthol sulphide cannot be qualitatively distinguished by means of its chemical behaviour from naphthathioxin; in fact, both exhibit the characteristic reactions of the thioxin structure, and, so far as our experiments have been carried, only minor quantitative differences in the reactivities of the two substances can be detected, the sulphur in the *iso*-derivative being somewhat less reactive than that in naphthathioxin. For these reasons it is clear that the thioxin structure for this anhydride must be adopted. It now remains to discuss the relative situation of the thioxin complex and the naphthalene nuclei. In previous papers it has been pointed out that since *iso*-β-naphthol sulphide is formed by reducing β-naphthasulphonium-quinone (VII), and is oxidised thereto by mild oxidising agents, the positions of oxygen and sulphur in this sulphide must be the same as in the quinone, that is, in the β- and α-positions respectively, as indicated by the following formula (VIII):



(VII.) (VIII.)

(IX.)

This arrangement is the same as that assigned for other reasons to β-naphthol sulphide (some of these are quoted in T., 1912, **101**, 1146, 1420). Without now discussing the ultimate structure of the *iso*-sulphide, it is sufficient to repeat that since the *iso*naphthathioxin is obtained from this by dehydration, it is to be expected that the thioxin arrangement which is formed should occupy the same situation (as in IX) as the several components. Other evidence leading to the αβ-structure for *iso*naphthathioxin may be adduced from the production of derivatives of this substance from β-naphthasulphonium-quinone (VII), which contains the sulphur and oxygen in these same positions. The quinone is almost quantitatively converted by cold acetyl bromide (this paper) or warm acetyl chloride (T., 1912, **101**, 715) into halogen derivatives of *iso*naphthathioxin. Reviewing these facts, it appears that there is as good evidence for accepting the αβ-structure for *iso*naphthathioxin as for naphthathioxin.

It may be further remarked that the dinaphthyl structure is not present in the *iso*-derivative because:

(1) This arrangement does not exist in the *iso*-sulphide, since that compound is converted * into the quinone by loss of only two atomic proportions of hydrogen. Moreover, the *iso*-sulphide is converted into β-naphthol sulphide by reaction with aqueous alkali hydroxide.

(2) Naphthathioxin is not converted into *iso*naphthathioxin by oxidation.

All the data thus lead to the conclusion that the skeletons of these two naphthathioxins are identical, and, if this is admitted, it appears impossible to find an explanation of the isomerism without some reference to the state of the naphthalene nuclei contained by the substances. It seems that the sole objection which can be offered against the identity of skeletal structure is the possibility that during the dehydration of either naphthol sulphide some shift of the thio- or oxygen groups may have taken place. In view of previous knowledge it seems highly improbable that such rearrangement should occur in naphthalene derivatives with reagents such as phosphoryl chloride at 100°, cold chlorosulphonic acid, or boiling acetic anhydride, which are those used to effect the dehydration. There is still less justification for assuming that in the formation of the *iso*-derivatives from naphthasulphonium-quinone rearrangement should take place with cold acetyl bromide or acetyl chloride. On general grounds, therefore, it seems that this objection against the $\alpha\beta$-structure for either substance cannot be urged with success.

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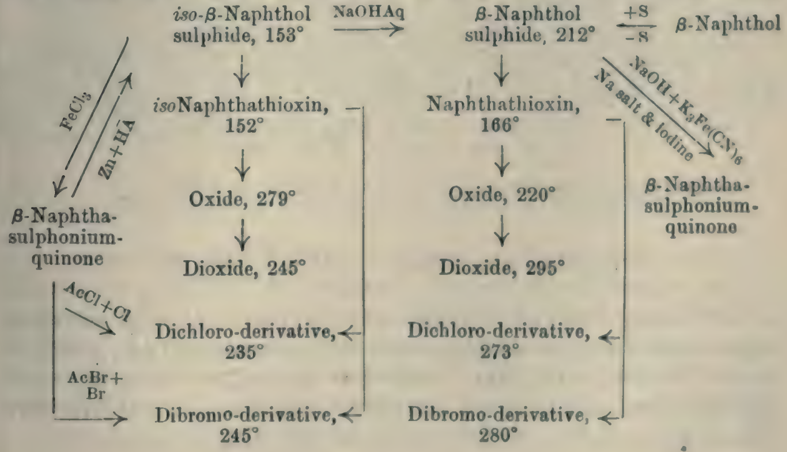
* Experiments proving this will be published in a subsequent paper.

Moreover, it may be remarked that to break up the thioxin complex requires much more violent reagents than those employed for dehydrating the sulphides, and hence it is difficult to provide analytical evidence which would be free from the same objection.

We do not, however, wish at present to make further deductions as to the nature of the isomerism of these substances, but prefer to postpone this until the case can be completed by inclusion of the parental sulphides in which the individual characteristics are more pronounced.

It may be of interest here to draw attention to the fact that perusal of the literature will show that already there are known several examples of isomeric naphthalene derivatives in which the substituents occupy the same positions; and a possible explanation of their nature has been foreshadowed by Willstätter (*Ber.*, 1911, **44**, 3431).

It remains, finally, to remark on the general relations existing in this group of substances; but a detailed description is unnecessary, since they are sufficiently evident from the accompanying



scheme. On inspection it will be clearly seen that there is an intimate relation on the one hand between the quinone and the *iso*-series, and on the other between the normal series and β-naphthol or β-naphthol sulphide.

The conclusions may be summarised as follows:

(1) Dehydration of *iso*-β-naphthol sulphide yields *iso*naphthathioxin, which possesses the simple molecular weight.

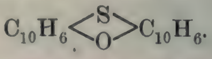
(2) This substance is isomeric with the naphthathioxin obtained by dehydration of β-naphthol sulphide; both substances contain the thioxin structure.

(3) Since the parental sulphides contain the thio- and oxygen groups in the α- and β-positions, it is inferred, with some reservation, that this arrangement is present in the anhydrides.

(4) The *iso*naphthathioxin is closely related to the naphthasulphonium-quinone.

## EXPERIMENTAL.

### *Derivatives of Naphthathioxin,*



$$C_{10}H_6{<}\begin{matrix}S\\O\end{matrix}{>}C_{10}H_6.$$

It is unnecessary now to describe the preparation of the parent substance of the group, for this has been previously dealt with in another paper (T., 1912, **101**, 714, and Mauthner, *loc. cit.*). In addition to the reactions mentioned in subsequent paragraphs, other characteristics of this naphthathioxin may now be described.

Ferric chloride added to the cold ethereal solution yields a green thioxonium double salt. The substance also is oxidised by cold concentrated sulphuric acid, a blue solution of the sulphoxide being formed. Moreover, when this naphthathioxin is boiled with a concentrated alcoholic solution of picric acid an insoluble reddish-brown picrate is formed; this is decomposed into the original components by treatment with aqueous alkali hydroxide.

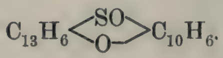
A cryoscopic determination of the molecular weight of naphthathioxin was made in molten naphthalene with the following result:

0·220 in 15 of naphthalene gave $\Delta = 0·345$. M.W. = 297.

$C_{20}H_{12}OS$ requires M.W. = 300.

The sample of naphthathioxin used melted at 166°.

### *Naphthathioxin Oxide,*



$$C_{13}H_6{<}\begin{matrix}SO\\O\end{matrix}{>}C_{10}H_6.$$

For the properties of this substance and the mode of preparation from naphthathioxin and nitric acid reference is made to a previous paper (T., 1912, **101**, 714). When a solution of the oxide (and hydrogen bromide) in acetic acid is warmed, the green thioxonium salt is precipitated.

### *Dichloronaphthathioxin*, $C_{10}H_5Cl<\substack{S\\O}>C_{10}H_5Cl$.

Naphthathioxin oxide was dissolved in hot glacial acetic acid, and then concentrated aqueous hydrogen chloride was added until a faint turbidity appeared. When the mixture was further warmed on the water-bath a mass of yellow needles was rapidly precipitated; and after these had ceased to accumulate, the solid was collected. Preliminary experiments showed that this substance was a mixture of mono- and di-chloronaphthathioxins which was very difficult completely to resolve by fractional crystallisation.

In order entirely to convert the material into the dichloro-compound it was re-chlorinated by a repetition of the foregoing process. Accordingly, the substance was converted into the mixture of oxides by means of concentrated nitric acid (see T., 1912, **101**, 714), and these were again treated with hydrogen chloride as described in the foregoing paragraph. The product formed an orange-coloured mass of needles, which contained a small quantity of nitrogenous material. In order to remove this impurity and some oxide of the dichloro-derivative which was possibly present, the material was dissolved in hot tetrachloroethane and reduced in this solution with a small quantity of acetic acid and zinc dust. After a few moments' action the solution was filtered and set aside to cool, when dichloronaphthathioxin separated in an almost pure condition. The substance was further purified by recrystallisation from tetrachloroethane, when it was finally obtained in large, lemon-yellow needles, which melted at 273°:

0·1070 gave 0·2540 $CO_2$ and 0·0282 $H_2O$. C = 64·7; H = 2·9.

0·1670 ,, 0·1303 AgCl. Cl = 19·3.

$C_{20}H_{10}OCl_2S$ requires C = 65·0; H = 2·7; Cl = 19·2 per cent.

*Dichloronaphthathioxin* imparts a green colour to warm sulphuric acid; it is sparingly soluble in most cold organic media, and is not further chlorinated by a hot mixture of hydrogen dioxide and hydrogen chloride in acetic acid.

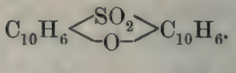
### *Dibromonaphthathioxin*, $C_{10}H_5Br<\substack{S\\O}>C_{10}H_5Br$.

A solution of naphthathioxin in warm glacial acetic acid was mixed with a solution of five atomic proportions of bromine in the same solvent. A copious, green precipitate of the thioxonium bromide then separated, but on continued warming on the water-bath this was finally converted into a yellow, crystalline solid. When the change was complete the solid was collected and purified by recrystallisation from hot tetrachloroethane:

0·1206 gave 0·2330 $CO_2$ and 0·0262 $H_2O$. C = 52·7; H = 2·4.
0·1548 „ 0·1276 AgBr. Br = 35·07.
$C_{20}H_{10}OBr_2S$ requires C = 52·4; H = 2·2; Br = 34·93 per cent.

*Dibromonaphthathioxin* obtained in this manner melted at 279—280°, and formed broad, well-defined, yellow needles. With warm sulphuric acid it gave the same colour reaction as the dichloro-derivative. When the substance was warmed with excess of bromine in acetic acid, no further bromination of the nucleus was observed.

### *Naphthathioxin Dioxide,*



$$C_{10}H_6\left<\begin{matrix}SO_2\\O\end{matrix}\right>C_{10}H_6.$$

The preparation of this substance from naphthathioxin by oxidation with potassium permanganate has been previously mentioned (T., 1911, **99**, 415); but since the product then obtained was obviously impure, the means by which the pure substance was made may now be given.

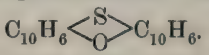
One gram of naphthathioxin was dissolved in warm acetic acid, and an equal weight of finely divided potassium permanganate was gradually added with shaking. When the action was complete the liquid was mixed with water, and then, after addition of sulphurous acid, the solid was collected and washed. At this stage a small quantity of the product was treated with concentrated sulphuric acid; the production of a blue colour indicates the presence of sulphoxide, and, if this was observed, the whole was submitted to renewed oxidation with half a gram of permanganate.

The substance was again isolated as before, and when dry was recrystallised first from acetic anhydride and finally from hot pyridine, from which it separated in colourless needles:

0·1018 gave 0·2698 $CO_2$ and 0·0337 $H_2O$. C = 72·27; H = 3·68.
$C_{20}H_{12}O_3S$ requires C = 72·29; H = 3·6 per cent.

Naphthathioxin dioxide is sparingly soluble in most organic media; it does not impart a colour to strong sulphuric acid, and when rapidly heated it melts at 293—295°.

### *Derivatives of* iso*Naphthathioxin:* iso*Naphthathioxin,*



$$C_{10}H_6\left<\begin{matrix}S\\O\end{matrix}\right>C_{10}H_6.$$

(*a*) For the preparation of this substance from the acetyl derivative of *iso*-*β*-naphthol sulphide and acetic anhydride reference is made to a previous paper (this vol., p. 340). No improvement to render the yields of the process more certain have been made. It may be added that when only small quantities of the thioxin have been formed they may be conveniently isolated from the bulk of the unchanged acetyl derivative by warming the whole with an alcoholic solution of picric acid. The insoluble picrate is then collected and decomposed in the usual manner. Instead of employing the acetyl derivative, the *iso*-sulphide may be used in this preparation.

(*b*) For the preparation from *iso*-β-naphthol sulphide and phosphoryl chloride reference is again made to a former paper (T., 1912, **101**, 1146). The product was identified by comparison with that given by the sulphuric acid method (see below). The yields are very poor.

(*c*) *From Chlorosulphonic Acid and* iso-β-*Naphthol Sulphide.*—Six grams of the sulphide were added in small portions to 25 grams of chlorosulphonic acid, which was kept at 0°. During the addition the solution was well stirred, and when all had been added the mixture was kept at the atmospheric temperature for fifteen minutes before being poured into a large bulk of ice-cold water. The subsequent isolation and purification were conducted as described below (*d*). The product was identified with that obtained by interaction of the sulphide and acetic anhydride [(*a*) and this vol., p. 340]. The yields are somewhat less than those obtained by the sulphuric acid method.

(*d*) *From Sulphuric Acid and* iso-β-*Naphthol Sulphide.*—Experiments dealing with the interaction of this sulphide with sulphuric acid have been previously described by Henriques (*Ber.*, 1894, **27**, 2999), who states that a dinaphthathiophen melting at 147° is obtained in yield of about 60 per cent. We have frequently repeated this experiment, but have never met with the thiophen derivative, obtaining instead the *iso*naphthathioxin in yields varying between 50 and 60 per cent. of the theoretical. The melting point of this product lies at about 147—148°, but it contains impurity, which is difficult entirely to remove, for the higher melting point (152°) of *iso*naphthathioxin prepared by the acetic anhydride method is reached only after prolonged crystallisation. In preparing the substance we have found most suitable the carefully described conditions adopted by Henriques, but it is advisable to use other means of purification. After the sulphuric acid solution has been mixed with water, the solid is collected and separately treated with excess of aqueous alkali hydroxide; it is then again collected and washed until free from alkali. The dry material is then extracted in a Soxhlet apparatus with hot benzene; this removes the required substance, leaving undissolved a small quantity of blue material. The latter is not easily removed by directly crystallising the crude material from acetic acid; but after extraction with benzene the product may be readily purified by recrystallisation from alcohol or acetic acid:

0·0964 gave 0·2824 $CO_2$ and 0·0361 $H_2O$. C=79·8; H=4·2.

$C_{20}H_{12}OS$ requires C=80·0; H=4·0 per cent.

The molecular weight was determined in molten naphthalene:

0·2134 in 15 of naphthalene gave $\Delta=0·340$. M.W.=292.

$C_{20}H_{12}OS$ requires M.W.=330.

The molecular weight of *iso*-β-naphthol sulphide, from which the anhydride was prepared, was also determined:

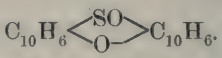
0·234 in 12·21 of benzene gave $\Delta=0·300$. M.W.=319.

$C_{20}H_{14}O_2S$ requires M.W.=318.

Analysis of the product obtained by the acetic anhydride method has been previously given (this vol., p. 348). The identity of the substance from the two sources was further established by (*a*) the identity of melting point (152°) taken alone or mixed with one another, (*b*) by conversion into the same dibromo-derivative (see later), and (*c*) by conversion to the same dioxide.

*iso*Naphthathioxin when pure does not immediately yield the blue colour with sulphuric acid, but after some time the colour gradually develops as oxidation to the sulphoxide proceeds. With naphthathioxin the production of the colour is almost instantaneous, and this shows that there is a slight difference in reactivity between the two substances. Other chemical behaviour of this *iso*naphthathioxin is similar to that already given for naphthathioxin; in fact, it is difficult qualitatively to distinguish the two substances. A mixture of *iso*naphthathioxin and naphthathioxin melts indefinitely at about 120°.

### iso*Naphthathioxin Oxide*,



$C_{10}H_6\left<\begin{matrix}SO\\O\end{matrix}\right>C_{10}H_6$.

(*a*) *Oxidation with Nitric Acid.*—Like the oxide of naphthathioxin, the *iso*-derivative may be prepared by the interaction of *iso*naphthathioxin with nitric acid (D 1·4). However, it is difficult to purify the product, for it contains nitrogen, not only as nitrate, but also attached to the nucleus. The method is therefore not to be recommended.

(*b*) *Oxidation with Hydrogen Dioxide.*—Two grams of *iso*naphthathioxin were mixed with 40 c.c. of warm acetic acid, and then 1·5 grams of hydrogen dioxide (30 per cent.) were added. On shaking the warm mixture, the remaining *iso*naphthathioxin dissolved, and in a short time the required substance began to separate. The reaction was completed by further warming, and the crystalline solid was finally collected (1·7 grams) from the cold liquid. The product was recrystallised from hot pyridine, in which it was readily soluble.

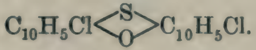
iso*Naphthathioxin* forms broad, colourless needles, which melt when rapidly heated at 278—279°; if this temperature is maintained a few moments after fusion, profound decomposition sets in:

0·1027 gave 0·2842 $CO_2$ and 0·0372 $H_2O$. C = 75·5; H = 4·0.

$C_{20}H_{12}O_2S$ requires C = 75·9; H = 3·8 per cent.

The substance gives an intensely blue solution with sulphuric acid. If aqueous hydrogen chloride is added to the solution in acetic acid the green colour of the thioxonium salt appears, but on warming this disappears, and gives place to a crystalline precipitate of a mixture of chloro-derivatives. On oxidation it is converted into the dioxide. These reactions indicate the presence of the thionyl group.

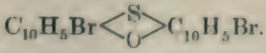
The nitrate is much more soluble than that of naphthathioxin oxide (T., 1912, **101**, 714).

### *Dichloro*iso*naphthathioxin*,  $C_{10}H_5Cl{<}\genfrac{}{}{0pt}{}{S}{O}{>}C_{10}H_5Cl$.

(*a*) *From β-Naphthasulphonium-quinone.*—The preparation of the substance from this source has already been fully described (T., 1912, **101**, 716).

(*b*) *From* iso*Naphthathioxin Oxide.*—The mode of preparation from the oxide by means of hydrogen chloride was the same as that described for dichloronaphthathioxin (see above). The product was identified with that made from the quinone (*a*) by means of the melting point of a mixture (235°).

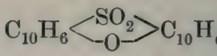
(*c*) *From* iso*Naphthathioxin.*—This substance was dissolved in hot acetic acid to which a small quantity of acetyl chloride had been added. Then hydrogen dioxide in slight excess of that required by theory was added. After the lapse of a few minutes more acetyl chloride was added to the hot mixture, which was then warmed on the water-bath for half an hour. The copious precipitate was collected and recrystallised from hot tetrachloroethane, when dichloro*iso*naphthathioxin was obtained in yellow, thread-like crystals, which melted at 235°, whether heated alone or mixed with a sample made from the quinone. (Found, C = 64·61; H = 2·9. $C_{20}H_{10}OCl_2S$ requires C = 65·0; H = 2·7 per cent.)

### *Dibromo*iso*naphthathioxin*,  $C_{10}H_5Br{<}\genfrac{}{}{0pt}{}{S}{O}{>}C_{10}H_5Br$.

(*a*) *From* iso*Naphthathioxin.*—The preparation from *iso*naphthathioxin obtained from the *iso*-sulphide with acetic anhydride has been fully described in a former paper (this vol., p. 349). The process has been carried out with a sample prepared by the sulphuric acid method, and the products from the two sources were identical (m. p. 245°).

(*b*) *From Naphthasulphonium-quinone.*—The same dibromo-derivative may be prepared from this quinone by (i) reaction with bromine in acetic anhydride, or (ii) bromination of the product obtained from the quinone and acetyl bromide. Full details of the processes have been previously given (this vol., p. 351). It is, however, important to add that on repeating the latter preparation (ii) we have been able to isolate the thioxonium bromide, which according to theory (see T., 1911, **99**, 976; 1912, **101**, 711) should be formed at the penultimate stage of the reaction. In these later experiments it was found that if the solution of the quinone in acetyl bromide was kept at the atmospheric temperature it solidified to a mass of the green thioxonium salt. This was collected, washed, and then boiled with acetic acid, when the impure monobromo*iso*naphthathioxin described in a previous paper was obtained. As before (this vol., p. 751) this melted at about 178°, and on analysis was found to contain from 1 to 1½ per cent. of bromine in excess of that required by theory. Bromination gave dibromo*iso*naphthathioxin.

### iso*Naphthathioxin Dioxide*,



$$C_{10}H_6<\begin{matrix}SO_2\\ O\end{matrix}>C_{10}H_6.$$

The preparation of this substance from (*a*) *iso*naphthathioxin or (*b*) the oxide thereof was conducted precisely as described above for naphthathioxin dioxide. It may be added that the same substance was obtained whether the thioxin employed had been made from the *iso*sulphide either with sulphuric acid or acetic anhydride. The product was crystallised first from acetic anhydride and then from hot pyridine:

0·1018 gave 0·2681 $CO_2$ and 0·0355 $H_2O$. C = 71·83; H = 3·8.

$C_{20}H_{12}O_3S$ requires C = 72·29; H = 3·6 per cent.

iso*Naphthathioxin dioxide* forms colourless plates, which melt at 244°. A mixture of this substance with naphthathioxin dioxide melted indefinitely between 225° and 235°.

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# XCIV.—*Studies of Dynamic Isomerism. Part XIV. Successive Isomeric Changes in Camphorcarboxylamide and Camphorcarboxypiperidide.*

By Thomas Martin Lowry and Walter Hamis Glover.

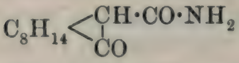
In nearly every case in which mutarotation curves have been examined, they have been found to conform more or less closely to the requirements of a simple unimolecular law. Special interest attaches therefore to the study of any substance which provides an exception to this well-established rule.

Preliminary observations of the amide and piperidide of camphorcarboxylic acid (P., 1910, **26**, 162) showed that these substances behaved in a totally different manner as compared with all that had been studied in previous papers of the present series. Our attention was specially attracted to a "period of induction," during which the rotatory power of the solutions remained practically constant, and to a "point of inflexion," which indicated that the velocity of change increased gradually to a maximum before the usual decrease of velocity set in.

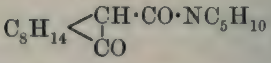
A mathematical investigation, carried out in collaboration with Mr. W. T. John (T., 1910, **97**, 2634), showed that curves possessing these characteristics might be produced by two successive isomeric changes, of which only the second was accompanied by any marked alteration of rotatory power. At the same time, however, the existence of certain very marked limitations was established. Thus it was discovered that the point of inflexion must occur at a very early stage of the action, since the maximum velocity must be reached before the change had proceeded to the extent of 26·4 per cent. of its total range. A similar limitation was found as regards the slope of the tangent at the point of inflexion. If the tangent were produced to cut the horizontal lines representing the initial and the final rotatory powers of the solution, it was shown that the ratio of the intercepts on these two lines could not in any circumstances exceed a maximum value of 0·0939.

These limiting figures were, however, exceeded in the case of the very first curves that were plotted for the mutarotation of the piperidide in benzene (see the full curves *a* and *b* of Fig. 2). Two curves were plotted, which coincided with one another with remarkable accuracy. These did not reach a point of inflexion until the change had covered some 35 per cent. of its total range, whilst the "ratio of the intercepts" was as high as 0·140. Whilst, therefore, the general character of the curves was similar to that which would be produced by two successive isomeric changes, it was clear that the cases which were being investigated were more complex, and probably involved more than two changes and more than three isomerides.

No difficulty was experienced in accounting for the complexity of these actions. In the paper in which they were first described (T., 1912, **101**, 1902), the amide and piperidide were represented by the conventional formulæ:

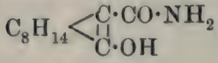

$C_8H_{14}<\begin{matrix}CH\cdot CO\cdot NH_2\\ |\\ CO\end{matrix}$

and

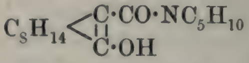

$C_8H_{14}<\begin{matrix}CH\cdot CO\cdot NC_5H_{10}\\ |\\ CO\end{matrix}$ . . (1) & (2)

Each of these formulæ, however, may represent either the α- or the α′-compound, a type of isomerism that has been fully investigated in the case of the halogen derivatives of camphor (Kipping, P., 1905, **21**, 125; Lowry, T., 1906, **89**, 1033).

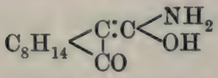
The enolic modifications:

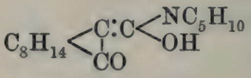

$C_8H_{14}<\begin{matrix}C\cdot CO\cdot NH_2\\ ||\\ C\cdot OH\end{matrix}$

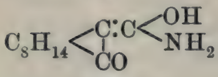
and

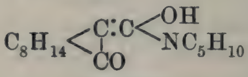

$C_8H_{14}<\begin{matrix}C\cdot CO\cdot NC_5H_{10}\\ ||\\ C\cdot OH\end{matrix}$ . . . . . (3)

(which provide the most obvious mechanism for the interconversion of the α- and α′-diketones formulated above) should exist in only one form; but this is no longer true of the enols of the hydroxymethylenecamphor type, each of which may exist in two well-defined stereoisomeric forms, thus:


$C_8H_{14}<\begin{matrix}C{:}C<\begin{matrix}NH_2\\ OH\end{matrix}\\ |\\ CO\end{matrix}$


$C_8H_{14}<\begin{matrix}C{:}C<\begin{matrix}NC_5H_{10}\\ OH\end{matrix}\\ |\\ CO\end{matrix}$ . . . . . (4)


$C_8H_{14}<\begin{matrix}C{:}C<\begin{matrix}OH\\ NH_2\end{matrix}\\ |\\ CO\end{matrix}$


$C_8H_{14}<\begin{matrix}C{:}C<\begin{matrix}OH\\ NC_5H_{10}\end{matrix}\\ |\\ CO\end{matrix}$ . . . . . (5)

Amide. Piperidide.

In addition to these five isomeric forms, three additional modifications are rendered possible in the case of the amide by converting the $\cdot CO\cdot NH_2$ group into $\cdot C(OH){:}NH$. As, however, the isomerism of the amide does not appear to be more complex than that of the piperidide, it is scarcely necessary to consider these in detail.

This multiplicity of possible isomerides is not altogether exceptional; for instance, dextrose and galactose may be represented by at least four formulæ, benzoylcamphor, hydroxymethylenecamphor, and aminomethylenecamphor by five formulæ analogous to those given above, and nitrocamphor might be represented in not less than seven different ways. In most cases, however, there are one or two isomerides, such as the normal and pseudo-forms of nitrocamphor, which predominate to such an extent that all the others may be left out of account in seeking to interpret the mutarotation phenomena. In the two cases now under consideration, there are evidently several isomerides which do not differ very greatly in stability or importance; the successive isomeric changes proceed with comparable velocities, and each exerts a distinct influence on the form of the mutarotation curve, as, for instance, in curve *f* (Fig. 2), where the effects of three such changes can be seen distinctly. The unusual precautions which have to be taken to crystallise out a homogeneous substance from such complex solutions are referred to later in the paper.

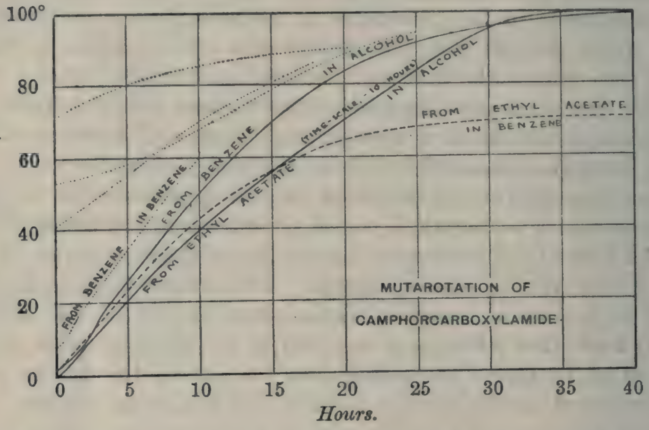
One further cause of complexity must be referred to at this point. The isomeric changes of the amide and piperidide appear to depend, as in the case of nitrocamphor, on the presence of traces of alkaline (?) impurities, apart from which the different isomerides would be quite stable even in solution. The relative quantities of the catalyst vary enormously, and exert a very large influence on the time-scale of the mutarotation curves. Thus in a clean silica tube, a solution of the piperidide in benzene gave a mutarotation curve, which showed that the change was half-complete in eighty hours; in a silica tube that had become contaminated with a trace of alkali, the corresponding period was reduced to three hours. A much more serious effect is seen in the influence of these impurities on the form (as distinguished from the scale) of the curves. The mutarotation curves for solutions of the piperidide in benzene always showed a well-marked period of induction, indicating clearly that the first of the successive changes was not accompanied by any marked alteration of rotatory power. The relative magnitude of the period of induction, however, varied considerably in the different curves; a solution which was observed in a clean silica tube showed a period of induction extending over two hours, the change being half-completed in 160 hours, a ratio of 1 to 80; in an alkaline silica tube the corresponding times were half an hour and three hours, and the ratio 1 to 6. The period of induction in the well-cleaned but still "dirty" tube is exaggerated by the gradual absorption of impurities, but it cannot be attributed entirely to this effect, as no such period was observed when alcohol or heptane was used as solvent, nor when experiments were made with the amide instead of the piperidide.

## EXPERIMENTAL.

### *Mutarotation of the Amide.*

Great difficulty was experienced in preparing the amide in such a form that only one of the isomerides was contained in the finished product. The pearly scales which usually separate from solution varied in rotatory power from $[\alpha]_{5461}$ +40° to +70°, and were evidently not homogeneous. It was hoped that homogeneous material might be obtained by soaking these minute crystals in heptane, and by extracting them repeatedly with this solvent; but when well-formed crystals of the amide were at last obtained from ethyl acetate by slow evaporation, it was found that these attempts had been unavailing, and that the pure amide was practically devoid of rotatory power. This conclusion was confirmed by the examination of crystals which had separated from benzene in well-formed tablets, but which became opaque too quickly to allow of goniometric examination; these were found, like the crystals from ethyl acetate, to be almost entirely inactive. Mutarotation curves for the crude amide, purified by ordinary methods and dissolved in alcohol, are shown by dotted lines in the upper portion of Fig. 1; the corresponding curves for homogeneous material, crystallised from benzene and from ethyl acetate and dissolved in alcohol as before, are shown by full lines in the same figure. The broken line shows the mutarotation of a homogeneous specimen of the amide, crystallised from ethyl acetate and dissolved in benzene; the dotted line in the lower part of the figure represents the mutarotation in benzene of a somewhat less pure specimen which had been prepared by allowing a solution in benzene to evaporate to dryness.

FIG. 1.



All the curves are marked by two characteristic features: (1) a long run during which the curve is either straight or much less curved than the unimolecular law would require; (2) an initial loop, in which the curve droops away from this line, but returns to it in the course of two or three hours. Both features point to the occurrence of successive isomeric changes. The initial loop appears to correspond with the period of induction of the piperidide, and suggests that the first product of change is a substance of relatively small rotatory power. The straightening out of the curve would result naturally from the occurrence of a series of changes, each accompanied by an increase of rotatory power. The effect would be to stimulate the growth of rotatory power by a fresh isomeric change, just as it was beginning to flag in view of the approaching completion of the preceding changes. Two successive changes would probably not suffice to account for the form of the curves, but it is evident that the appearance of a third or fourth product of change might stimulate the growth of rotatory power at still later periods, and so keep the curve nearly straight almost to the end of the action.

The numerical data for the three most important curves are reproduced in table I:

TABLE I.—*Mutarotation of Camphorcarboxylamide.*

(*a*) *Cryst. Ethyl Acetate, Diss. Alcohol* (5 grams/100 c.c.)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hours) | 0·1 | 0·2 | 0·3 | 0·4 | 0·5 | 0·6 | 0·8 | 1·0 | 1·5 | 2·0 | 2·5 |
| $[\alpha]_{5461}$ | −0·2 | +0·1 | 0·2 | 0·3 | 0·4 | 0·6 | 1·1 | 1·4 | 2·5 | 3·7 | 4·8° |
| Time (hours) | 3·0 | 3·5 | 4·0 | 4·5 | 5·0 | 8·0 | 9·0 | 10·0 | 11·0 | 12·4 | 14·2 |
| $[\alpha]_{5461}$ | 5·9 | 7·1 | 8·2 | 9·4 | 10·4 | 17·2 | 19·0 | 21·0 | 23·3 | 25·8 | 29·3° |
| Time (hours) | 22 | 26 | 30 | 33 | 34 | 36 | 48 | 50 | 51 | 52 | 53 |
| $[\alpha]_{5461}$ | 43·4 | 50·3 | 56·4 | 60·7 | 62·3 | 64·8 | 81·1 | 84·0 | 85·4 | 86·5 | 88·3° |
| Time (hours) | 54·5 | 56 | 58 | 59·4 | 61 | 71 | 83 | Final | | | |
| $[\alpha]_{5461}$ | 90·3 | 91·8 | 93·8 | 94·7 | 96·0 | 99·6 | 100·4 | 100 8° | | | |

(*b*) *Cryst. Benzene, Diss. Alcohol* (5 grams/100 c.c.).

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hours) | 0·1 | 0·2 | 1·0 | 2·4 | 3·1 | 3·5 | 4·0 | 4·5 | 4·8 | 6·0 | 7·0 |
| $[\alpha]_{5461}$ | +2·3 | 2·7 | 4·5 | 11·8 | 16·8 | 19·2 | 21·6 | 24·3 | 25·9 | 31·4 | 36 9° |
| Time (hours) | 7·4 | 8·0 | 9·0 | 12·4 | 15·4 | 17·6 | 19·0 | 20·1 | 21·0 | 22·0 | 24·0 |
| $[\alpha]_{5461}$ | 38·3 | 41·3 | 46·5 | 60·4 | 70·7 | 77·3 | 80·4 | 84·0 | 85·5 | 87·4 | 90·1° |
| Time (hours) | 25 | 26 | 28 | 30 | 32 | 42 | Final | | | | |
| $[\alpha]_{5461}$ | 91·3 | 92·9 | 94·7 | 96·0 | 97·0 | 99·6 | 100·6 | | | | |

(*c*) *Cryst. Ethyl Acetate, Diss. Benzene* (5 grams/100 c.c.).

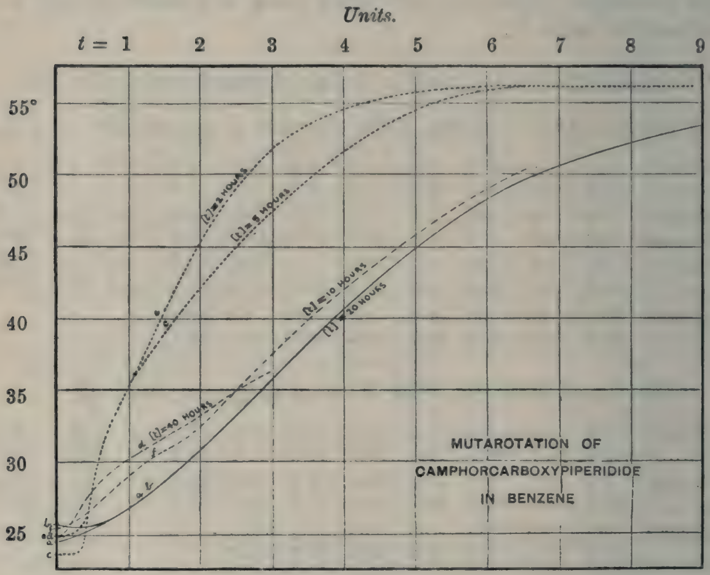
| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hours) | 0·1 | 0·2 | 0·4 | 0·6 | 0·8 | 1·0 | 2·0 | 3·0 | 4·0 | 5·0 | 6·0 | 7·0 |
| $[\alpha]_{5461}$ | 1·5 | 2·0 | 2·9 | 3·6 | 4·7 | 5·5 | 10·1 | 15·0 | 19·9 | 24·1 | 28·7 | 32·6° |
| Time (hours) | 8·0 | 10·0 | 12·0 | 13·3 | 23·0 | 25·0 | 28·4 | 31·0 | 36·0 | 48·0 | 61·0 | 96·0 |
| $[\alpha]_{5461}$ | 36·5 | 43·4 | 49·2 | 52·4 | 67·4 | 68·0 | 69·7 | 71·0 | 70·9 | 72·7 | 73·8 | 74·4° |

### *Mutarotation of the Piperidide.*

The first experiments on the mutarotation of the piperidide were made with material which had been crystallised from alcohol, then dissolved in clean benzene, and transferred to a clean silica polarimeter tube for observation. Two series of experiments were made, as shown by the data of table II (*a*) and (*b*), and the full curves of Fig. 2. After the first few hours the curves run together with a closeness that is quite exceptional in work of this kind. The curves are particularly smooth and regular in appearance, with a well-marked period of induction; it was, indeed, the graceful character of these two curves that supplied the inducement to undertake the mathematical investigation already referred to.

The well-marked, crystalline character of the piperidide used in these first experiments created the impression that no important alteration would be effected by recrystallising the substance from ethyl acetate and using the well-formed crystals (prepared with far greater ease than in the case of the amide) for the mutarotation experiments. This anticipation was not realised. The initial specific rotatory power of the homogeneous crystals was, indeed, practically the same as that of the less well-defined material that had separated from alcohol. The mutarotation curves, however, differed in a remarkable degree, and showed conclusively that the constancy of specific rotatory power was not due to the complete purity of the earlier material, but to the fact that the isomeride that had been carried down with the crystals was substantially identical in specific rotatory power with the main constituent; the existence of such an isomeride had already been shown to be neces-

Fig. 2.



sary to explain the occurrence of a period of induction in these solutions.

Homogeneous material was finally prepared by crushing the well-formed crystals that had separated from ethyl acetate, stirring for several hours with heptane, draining, and drying in the air. Two entirely distinct samples were used, and each solution was examined both in a clean glass polarimeter tube and in a silica tube that had become fouled with alkali. The rapid mutarotation in the foul silica tube is shown by the dotted curves of Fig. 2 and the numbers given in table II (*c*) and (*e*). The glass tube, which appears to have been exceptionally clean, gave the slow mutarotation curves represented by the broken lines of Fig. 2 and the data of table II (*d*) and (*f*).

### TABLE II.

*Mutarotation of Camphorcarboxypiperidide.*

(a) *Cryst. Alcohol, Diss. Benzene* (5 grams/100 c.c.), *Clean Silica Tube.*

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hours) | 0·05 | 0·6 | 1·0 | 2·5 | 5·3 | 11·0 | 24·0 | 34·5 | 46·0 | 59 0 | 70·5 |
| $[\alpha]_{5461}$ ........ | +24·3 | 24·1 | 24·4 | 24·7 | 24·8 | 25·8 | 27·8 | 30·3 | 31·8 | 36·3 | 39·0° |

(b) *Repetition of* (a), *with Same Specimen of Piperidide.*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Time (hours) | 0·1 | 0·4 | 2 | 9 | 12 | 24 | 30 | 36 | 48 | 54 |
| $[\alpha]_{5461}$ ........ | 25·8 | 25·5 | 25·5 | 25·3 | 25·6 | 27·7 | 28·7 | 29·9 | 32·9 | 34·2° |
| Time (hours) | 61 | 72 | 78 | 84 | 96 | 108 | 132 | 144 | 156 |
| $[\alpha]_{5461}$ ........ | 36·2 | 39·1 | 40·6 | 42·2 | 44·2 | 46·5 | 49·8 | 51·2 | 51·2° |
| Time (days) | 7 | 7·5 | 8 | 8·5 | 9 | 10 | 15 | 21 | 40 |
| $[\alpha]_{5461}$ ........ | 52·9 | 54·3 | 54·7 | 54·8 | 54·8 | 55·6 | 56·3 | 56·9 | 56·7° |

(c) *Cryst. Ethyl Acetate, Diss. Benzene* (5 grams/100 c.c.), *Foul Silica Tube.*

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hours) | 0·4 | 0·6 | 1·0 | 1·5 | 2·0 | 2·1 | 2·2 | 2·3 | 2·5 | 2·9 | 3·6 |
| $[\alpha]_{5461}$ ........ | 23·5 | 23·5 | 23·5 | 24·0 | 24·7 | 26·2 | 27·0 | 28·0 | 28·5 | 29·9 | 32·2° |
| Time (hours) | 3·9 | 4·5 | 4·9 | 5·5 | 6·0 | 6·5 | 7·0 | 8·0 | 9·0 | 10·0 | 11·0 |
| $[\alpha]_{5461}$ ........ | 33·0 | 33·8 | 35·4 | 37·3 | 37·4 | 38·0 | 38·8 | 40·2 | 41·0 | 42·1 | 43·5° |
| Time (hours) | 12·0 | 12·9 | 20 | 22 | 23 | 26 | 28 | 30 | 33 | 36 | 47 |
| $[\alpha]_{5461}$ ........ | 44·3 | 45·3 | 51·9 | 52·8 | 53·5 | 55·0 | 55·6 | 55·9 | 56·1 | 56·4 | 56·3° |

(d) *Same Solution, Clean Glass Tube.*

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hours) | 0·5 | 0·7 | 1·0 | 1·5 | 2·0 | 2·3 | 2·5 | 3·0 | 3·5 | 4·0 | 4·5 | 5·0 |
| $[\alpha]_{5461}$ ........ | 24·7 | 24·7 | 24·7 | 24·7 | 25·0 | 25·3 | 25·3 | 25·4 | 25·6 | 25·8 | 25·7 | 25·6° |
| Time (hours) | 5·5 | 6·5 | 8·0 | 9·0 | 10·0 | 11·0 | 12·0 | 13·0 | 22 | 28 | 30 | 33·1 |
| $[\alpha]_{5461}$ ........ | 25·6 | 25·8 | 26·3 | 26·5 | 26·6 | 27·0 | 27·1 | 27·5 | 28·0 | 29·0 | 29·2 | 29·6° |
| Time (hours) | 36 | 46·8 | 54 | 59 | 70 | 73 | 78 | 84 | 94 | 102 | | |
| $[\alpha]_{5461}$ ........ | 30·0 | 30·9 | 31·3 | 31·6 | 32·4 | 32·6 | 33·3 | 33·7 | 34·4 | 35·4° | | |

(e) *Cryst. Ethyl Acetate, Diss. Benzene* (5 grams/100 c.c.), *Foul Silica Tube.*

| Time (hours) | 0·5 | 0·6 | 0·75 | 0·9 | 1·0 | 1·1 | 1·2 | 1·4 | 1·5 | 1·7 | 2·0 | 2·5 | 3·0 | 4·1 | 4·3 | 4·5 | 5·0 | 6·0 | 7·0 | 8·0 | 22·5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $[\alpha]_{5461}$········ | 25·0 | 25·4 | 26·3 | 27·1 | 28·4 | 29·2 | 30·1 | 31·9 | 32·2 | 33·7 | 35·5° | 38·8 | 40·8 | 45·4 | 46·2 | 47·3 | 49·1 | 51·9 | 53·5 | 54·6 | 56·5° |

(f) *Same Solution, Clean Glass Tube.*

| Time (hours) | 0·5 | 0·6 | 0·7 | 1·0 | 1·5 | 2·0 | 3·0 | 4·6 | 6·0 | 8·0 | 10·0 | 21·0 | 22 | 27 | 33 | 42·5 | 49 | 53 | 65 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $[\alpha]_{5461}$········ | 25·4 | 25·5 | 25·4 | 25·2 | 25·3 | 25·2 | 25·4 | 26·4 | 27·0 | 28·2 | 31·4° | 32·8 | 33·4 | 36·1 | 39·3 | 43·1 | 45·4 | 46·6 | 50·2° |

The first solution changed much more slowly than the second in both tubes; but by using different time-scales the curves are brought closely together, and show a very satisfactory agreement in the behaviour of the two samples. The two dotted curves, which represent the rapid mutarotation in the dirty tube, show a very conspicuous period of induction, followed by a period in which the change of rotatory power proceeds with extraordinary rapidity; the remaining portions of the curves show the long, straight run, to which attention has already been directed in the case of the amide, after which the change of rotatory power soon ceases. The two broken curves, showing the slow changes of rotatory power in the glass tube, were not followed to completion, although readings were taken during a period of several days. They show, however, a very important feature, which can scarcely be detected in the two rapid curves, and is altogether obliterated from the full curve for the non-homogeneous material crystallised from alcohol; this feature consists in the appearance of two distinct periods of acceleration, and affords conclusive evidence that the mutarotation is not due merely to one or two isomeric changes, but involves at least three successive changes in the piperide, which must therefore exist in at least four isomeric forms. These changes give rise:

(1) to a period of induction, during which the first form is changing into a second form of equal rotatory power;

(2) a period of acceleration and subsequent retardation, marking the rise and fall of a third isomeride of higher rotatory power;

(3) a second period of acceleration, due to the production of a fourth isomeride of still higher optical activity.

The second period of acceleration is followed by a "straight-run," which may perhaps be caused by the appearance of a fifth isomeride, but on this point it would be unwise to speak dogmatically.

A few experiments were made on the mutarotation of the piperidide in alcohol. The curves appeared to be approximately normal in shape, but the change of rotatory power from $[\alpha]_{5461}$ +112° to +118° was so small that it was not possible to determine accurately the exact course of the mutarotation.

## *Improved Methods for Measuring Changes of Solubility.*

The increase of solubility with time was measured in the case of both substances in order to determine the proportion of the most stable form that was present in the final equilibrium. Important improvements on the methods previously in use were effected.

(1) By crystallising the substance from ethyl acetate in order to secure well-crystallised, homogeneous material, and at the same time to eliminate basic impurities, such as ammonia, by converting them into inert products, such as acetamide.

(2) By using Kahlbaum's commercial heptane as solvent; this has the advantage of being chemically inactive and readily freed from moisture and basic impurities by distilling from phosphoric oxide; as compared with the light petroleum previously employed (T., 1904, **85**, 1546), it is more homogeneous and less liable to evaporate during stirring and filtration, but still sufficiently volatile to allow the filtered solutions to be evaporated without undue heating.

(3) By adding the finely-powdered solid at intervals of a few seconds, and in quantities of a few centigrams, to the vigorously-stirred solvent through an aperture in the cork at the top of the tube; under these conditions the finer particles, which usually disappear in the first stages of the dissolution, are retained for use in the process of saturation; complete saturation may thus be secured in the course of two minutes, and only a small excess of the solid need be employed.

## *Solubility of Amide.*

Very great difficulty was experienced in preparing the amide in a homogeneous form suitable for experiments on solubility.

The first experiments were made with amide crystallised from light petroleum. Three successive extractions gave the following solubilities:

| | | | | |
|---|---|---|---|---|
| Initial ...... | 0·60 | Final......... | 0·80 | Grams of amide per 100 grams of heptane. |
| ,, ...... | 0·73 | ,, ......... | 0·79 | |
| ,, ...... | 0·38 | ,, ......... | 0·74 | |

In the third experiment observations were made at short intervals after mixing the amide with the solvent, as the change was evidently a rapid one; the actual figures were: 10 min., 0·41; 20 min., 0·46; 40 min., 0·53; 80 min., 0·68; 160 min., 0·75; 280 min., 0·73; whence by extrapolation 0 min., 0·38. As the material for the third experiment had been stirred for several days with two successive quantities of heptane, then drained, and again washed with heptane, it was thought that the initial value might be accepted as representing the true solubility of the pure homogeneous unchanged amide. It was not, indeed, until experiments with well-formed crystals had reduced the initial value to 0·24 per cent. that the extreme difficulty of securing homogeneous material was realised. This difficulty is shown by a second series of experiments, in which 10 grams of a new sample, which had been purified most carefully by ordinary methods and finally crystallised out from light petroleum, were soaked with heptane for two months before use. Two grams of the product were stirred with heptane during two days, drained, washed, and powdered; again extracted for two days, drained, washed, and powdered; finally half a gram only of the powder, stirred with 200 c.c. of heptane, gave the following values:

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time......... | 5 m. | 10 m. | 20 m. | 0·5 d. | 2·5d. | 7·5 d | 14·5 d | 50 d. | 56 d. | 56 d. | Final |
| Solubility.. | 0·35 | 0·37 | 0·38 | 0·48 | 0·48 | 0·60 | 0·64 | 0·75 | 0·76 | 0·79 | 0·77 |

The remainder of the 2 grams was soaked with heptane during another sixty days, drained, powdered, extracted twice with heptane, again drained, and then gave the following initial values:

| | | | |
|---|---|---|---|
| Time ......... | 0 m. | 6 m. | 12 m. |
| Solubility ... | [0·26] | 0·29 | 0·32 |

| | | | |
|---|---|---|---|
| Time......... | 0 m. | 6 m. | 12 m. |
| Solubility.. | [0·26] | 0·31 | 0·36 |

These values agree with those observed when using well-formed crystals, but this agreement was only obtained after operations extending over a period of more than four months.

Experiments with crystals which had separated from ethyl acetate easily gave concordant initial values, but the final values were reached with extreme slowness on account of the efficiency of this solvent in removing the last traces of catalyst from the crystals. The first specimen gave high values for the first two extractions; a third extraction gave during the first twenty minutes the values 0·20, 0·27, 0·32, 0·25; mean, 0·26. A fourth extraction gave:

| | | | | | | |
|---|---|---|---|---|---|---|
| Time......... | 5 m. | 10 m. | 20 m. | 2 h. | 56 h. | Initial |
| Solubility.. | 0·24 | 0·23 | 0·25 | 0·30 | 0·42 | 0·24 |

A second sample gave at the third extraction: 16 min., 0·27; two hours, 0·29; final (several days later), 0·68; at the fourth extraction: 6 min., 0·23; 12 min., 0·23; 18 min., 0·24. A third sample gave at the first extraction of the whole quantity: 5 min., 0·23; 10 min., 0·24; at a second extraction: 5 min., 0·25; at a third and fourth extraction:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time ......... | 5 m. | 10 m. | 15 m. | 20 m. | 30 m. | 4 d. | Initial |
| Solubility ... | 0·25 | 0·24 | 0·25 | 0·24 | 0·25 | 0·59 | 0·24 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time ......... | 1 d. | 2 d. | 3 d. | 4 d. | 11 d. | 17 d. | 89 d. | Final |
| Solubility ... | 0·27 | 0·34 | 0·42 | 0·46 | 0·61 | 0·65 | 0·66 | 0·66 |

A fourth sample, which had already given correct initial values, 5 min., 0·24; 10 min., 0·23, was extracted (*a*) with pure heptane, (*b*) with heptane containing a trace of ammonia:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (*a*) | Without ammonia | Time ...... | 5 m. | 1 d. | 3 d. | 7 d. | 18 d. | 37 d. | Final |
| | | Solubility . | 0·24 | 0·54 | 0·64 | 0·66 | 0·64 | 0·65 | 0·65 |
| (*b*) | With ammonia | Time ......... | 1 d. | 3 d. | 7 d. | 18 d. | — | | Final |
| | | Solubility ... | 0·53 | 0·58 | 0·59 | 0·66 | — | | 0·66 |

It will be noticed that the ammonia, which was added with an additional quantity of heptane at the end of one day, makes very little difference to the rate of change, but as this particular sample happened to combine a low initial solubility with a rapid rate of change it served to establish finally the correctness of the following values:

| | |
|---|---|
| Initial solubility.................. | 0·24 |
| Final solubility .................. | 0·66 |
| Ratio .............................. | 0·36 |

### *Solubility of Piperidide.*

The determination of the ratio of the initial to the final solubility proved to be quite as tedious and difficult as in the case of the amide, several score of observations being made with different samples over a period of two years. It will be sufficient, however, to give the data for the last series, by which the ratio was finally established. The following values are for six successive extractions of the carefully-purified sample:

| | | | | | | |
|---|---|---|---|---|---|---|
| 5 m. | 1·83 | 5 m. | 1·90 | 5 m. | 1·83 | Initial solubility 1 87 |
| 10 m. | 1·85 | 10 m. | 1·88 | 15 m. | 1·89 | |
| 5 m. | 1·88 | 5 m. | 1·87 | 10 m. | 1·89 | |
| 15 m. | 1·85 | 15 m. | 1·94 | 25 m. | 1·92 | |

The following values are in continuation of the last extraction:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (*a*) | Without piperidine | 1 d. | 3 d. | 6 d. | 16 d. | 21 d. | 24 d. | 30 d. | Final |
| | | 2·00 | 2·05 | 2·56 | 4·19 | 4·12 | 4·24 | 4·26 | 4·20 |
| (*b*) | With piperidine | 1 d. | 2 d. | 4 d. | 7 d. | 17 d. | 22 d. | 25 d. | Final |
| | | 2·26 | 2·90 | 3·86 | 4·12 | 4·24 | 4·14 | 4·12 | 4·16 |

In view of the fact that the solution with piperidine was changing several times more quickly than the solution to which no piperidine was added, it was considered safe to assume that the final solubility had been reached when the two curves came together at the end of about a fortnight. After longer periods the piperidide appeared to undergo some permanent decomposition, giving rise to solubility values very considerably higher than those recorded above; but as the solution with piperidine gave steady values from seven to twenty-five days, no large error is likely to be introduced by taking as the correct values for the piperidide:

| | |
|---|---|
| Initial solubility | 1·87 |
| Final solubility | 4·18 |
| Ratio | 0·45 |

The last series of values was more trustworthy than the earlier ones because care was taken to evaporate the solutions at so low a temperature that the piperidide separated in crystals, instead of remaining as a fused or gelatinous mass; it is believed that this point is of some importance in securing accurate weighings.

It should also be added that the difficulty of securing homogeneous material is closely associated with the inflected character of the mutarotation curves; both phenomena are dependent on the existence of several dynamic isomerides of approximately equal stability and on the occurrence of several successive isomeric changes proceeding so slowly as to exert a marked influence on the properties and behaviour of the solutions.

## *Summary and Conclusions.*

(1) The amide and piperidide of camphorcarboxylic acid give rise to mutarotation curves of remarkable complexity.

(2) This is attributed to the occurrence of at least three successive isomeric changes, involving not less than four isomerides.

(3) The shape, as well as the scale, of the mutarotation curves may be altered by the gradual absorption of a catalytic impurity.

(4) Solubility measurements have shown that the original form persists after dissolution to the extent of about 36 per cent. in the case of the amide and 45 per cent. in the case of the piperidide.

The authors are indebted to the Research Funds of the Chemical Society and of the British Association for grants which have defrayed a part of the cost of the investigation. They desire also to acknowledge the valuable assistance of Mr. H. R. Courtman in carrying the research through its final stages.

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## XCV.—*Quinonoid Addition as the Mechanism of Dyestuff Formation.*

By Arthur George Green.

In 1899 Thiele (*Annalen*, 1899, **306**, 132) advanced an explanation of the capacity for addition exhibited by quinones and quinonoid compounds which was based on his theory of unsaturation and the existence in such compounds of a chain of "conjugate" double linkings. Bucherer in 1907 (*Ber.*, **40**, 3412) further developed this hypothesis, referring to a single type all the reactions by which the dyestuffs of the azine, thiazine, and oxazine series are produced (compare Möhlau and Bucherer, "Farbenchemisches Praktikum"). For some time past I have employed a similar generalisation, of a somewhat more comprehensive character, which appears to supply a ready explanation of the mechanism by which complex dyestuff molecules are built up, not only in the above-mentioned classes, but also in other groups in which substitutive changes are usually assumed (for example, the rosaniline group).

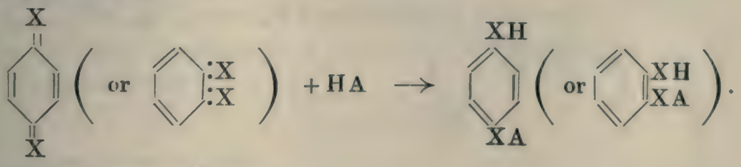
In view of the assistance which such generalisations afford to the student of dyestuff chemistry I venture to give the following account of the form in which I employ this hypothesis.

(1) All quinones and quinone-like compounds, by reason of their high degree of "unsaturation," exhibit a great attraction for hydrogen or equivalent groups, by the assumption of which they can pass into more saturated compounds.

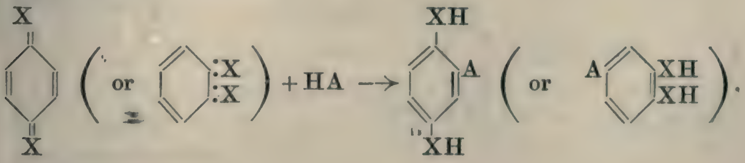
(2) A very large proportion of dyestuff syntheses and the individual steps in such syntheses may be represented as consisting in the linking up of molecules ("Verkettungen") brought about through the attractive forces of quinonoid groups.

(3) Such reactions may occur in two ways, namely:

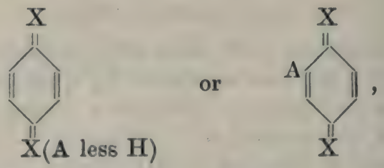
(*a*) Direct Addition:



(*b*) Indirect Addition:



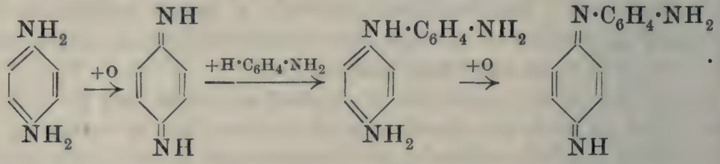
(4) In the presence of an oxidising agent, such as chromic acid, a chlorate, atmospheric oxygen, or another quinonoid compound, the above additive products are again converted into quinonoid derivatives,



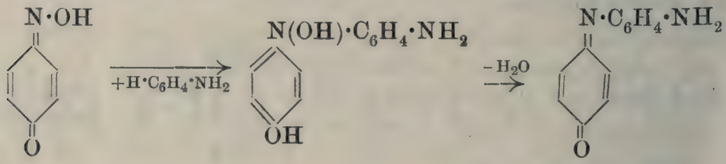
which under suitable conditions are ready to react again in the same way, with production of compounds of still greater complexity. Such alternate additions and reoxidations may occur several times in succession, thus producing (as in the aniline-black and induline series) very complex molecular structures.

## *Direct Quinonoid Addition.*

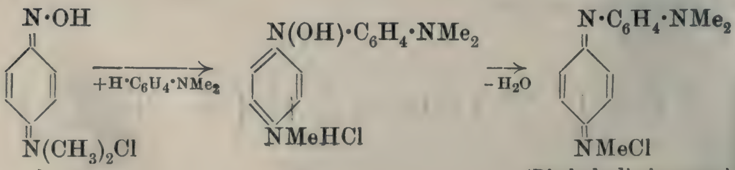
Simple examples of reactions of this type are seen in the formation of the indamines and indophenols by conjoint oxidation of para-diamines or para-aminophenols with amines or phenols. Taking phenylene-blue as typical of these compounds, the reactions occurring may be represented as follows:



The formation of indamines or indophenols from nitrosoamines or nitrosophenols can also be represented in a similar manner:

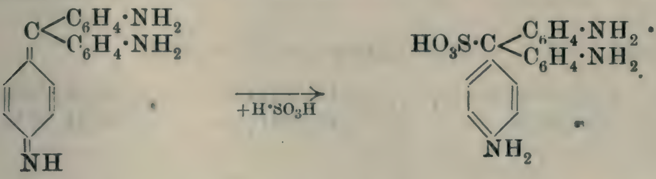


(Simplest indophenol.)



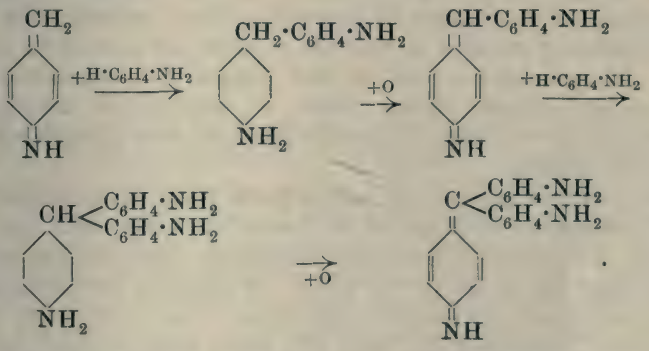
(Bindschedler's green.)

The tendency of the triphenylmethane dyestuffs to form colourless compounds by combination with sulphurous acid, hydrogen cyanide, water, etc., has been represented by Thiele as follows:



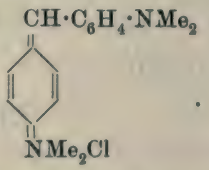
$C<\begin{smallmatrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{smallmatrix}$
NH
+H·SO₃H
$HO_3S\cdot C<\begin{smallmatrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{smallmatrix}$
NH₂

Most of the reactions which lead to dyestuffs of the triphenylmethane group can be better explained as additive processes than by the ordinary method of representation; thus the formation of pararosaniline by oxidation of a mixture of *p*-toluidine and aniline may be represented by assuming that the former is first oxidised to the carboquinonimide which then reacts with aniline in the following manner:

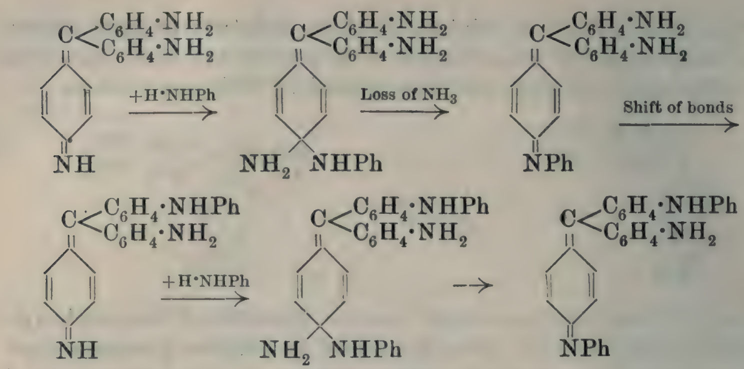


CH₂
NH
+H·C₆H₄·NH₂
CH₂·C₆H₄·NH₂
NH₂
+O
CH·C₆H₄·NH₂
NH
+H·C₆H₄·NH₂
$CH<\begin{smallmatrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{smallmatrix}$
NH₂
+O
$C<\begin{smallmatrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{smallmatrix}$
NH

The hydrol and carbonyl chloride syntheses of triphenylmethane dyestuffs may also be regarded in a similar light; thus the extraordinary facility with which tetramethyldiaminobenzhydrol undergoes condensation with a wide range of substances is explained if we attribute these reactions to the additive capacity of the hydrol salt in its quinonoid form:



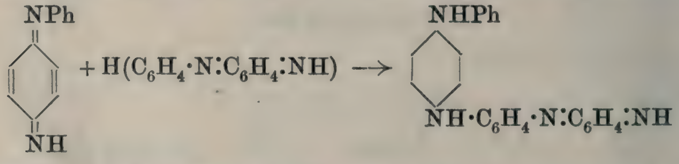
Even the phenylation of rosaniline in the production of aniline-blue may be regarded with great probability as a quinonoid reaction, although of a different type from the above:



and so on.

This method of representation accounts for the readiness with which phenylation takes place compared with the ordinary phenylation of amines, and also explains the function of the benzoic acid used. This weak acid preserves a sufficient degree of acidity to determine the elimination of ammonia without retaining the latter in the reacting mixture, so that the reaction can proceed to completion. If hydrochloric acid is used instead, the accumulation of ammonium chloride brings about an equilibrium, through the reversal of the reaction, when only the mono- or di-phenylated stage has been reached.

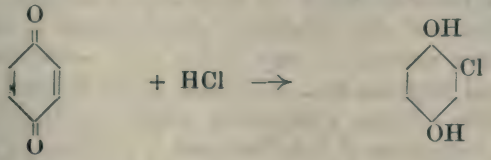
Recent investigations on aniline-black have demonstrated that the intermediate products of its formation, emeraldine and nigraniline, are complex indamines containing eight aniline residues linked together in the para-position. A study of the formation of these compounds (Willstätter and Moore, *Ber.*, 1907, **40**, 2665; Green and Woodhead, T., 1910, **97**, 2388) makes it very probable that the mechanism of their formation is as follows: The first oxidation product of aniline capable of isolation is the yellow phenylquinonimide of Caro. This substance, under the influence of mineral acids, is at once converted into the blue imide of Willstätter, a reaction which consists in the direct addition of one molecule of the yellow imide to the quinonoid groups of a second:

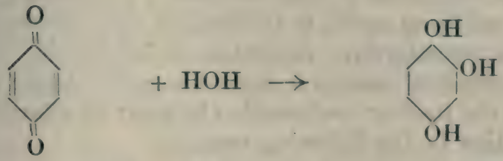


Further oxidation of the blue imide gives the red imide of Willstätter, $NPh:C_6H_4:N \cdot C_6H_4 \cdot N:C_6H_4:NH$, and this also under the influence of mineral acids undergoes a similar addition and produces nigraniline. Or the blue imide may, by addition to the red imide, produce emeraldine, which latter on oxidation gives nigraniline. The tendency to the formation of such complex molecules is thus readily explained.

### *Indirect Quinonoid Addition.*

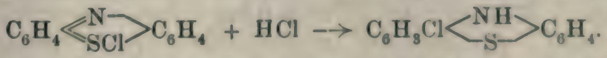
Simple examples of indirect quinonoid addition are to be found in the convertion of *p*-benzoquinone into chloro- or hydroxy-quinol by the action of hydrochloric acid or of sodium hydroxide respectively (Barth and Schreder, *Ber.*, 1879, **12**, 417, 503):





An important case in which the latter reaction occurs is the formation of dihydroxyanthraquinone (alizarin) by alkali fusion of anthraquinonemonosulphonic acid or even of anthraquinone itself, and a similar introduction of hydroxyl probably constitutes an intermediate stage in the production of indanthren-blue by the alkaline fusion of 2-aminoanthraquinone. Thiele (*Ber.*, 1898, **31**, 1247; *Annalen*, 1900, **311**, 341) has also found that acetyl derivatives of chloro- or hydroxy-quinol are readily formed from *p*-benzoquinone by the action of zinc chloride or concentrated sulphuric acid respectively in the presence of acetic anhydride. A similar reaction has been described by Schultz (*Ber.*, 1882, **15**, 652), who obtained diacetyldichloroquinol by the action of acetyl chloride on *p*-benzoquinone.

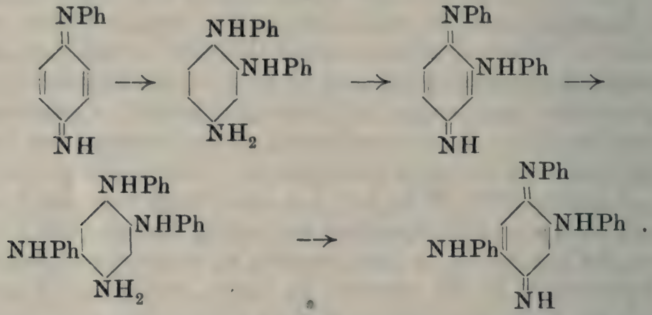
Many analogous cases have been observed amongst orthoquinonoid dyestuffs; thus Page and Smiles (T., 1910, **97**, 1112) have observed the ready formation of chloro-compounds from phenazothionium salts when heated with hydrochloric acid:



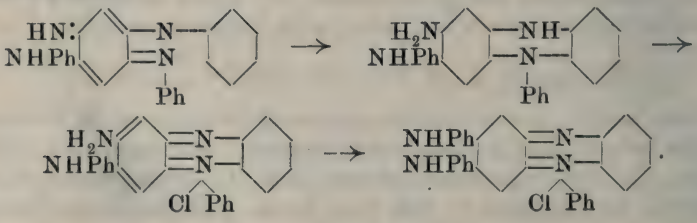
$$C_6H_4{<}^{N}_{SCl}{>}C_6H_4 + HCl \rightarrow C_6H_3Cl{<}^{NH}_{S}{>}C_6H_4.$$

Other simple cases of indirect quinonoid addition are to be found in the formation of *p*-phenylenediaminesulphonic acid, and of the mono-, di-, and tetra-thiosulphonic acids of *p*-phenylenediamine obtained by oxidation of this base in the presence of sulphurous or thiosulphuric acids (compare Green and Perkin, T., 1903, **83**, 1201). Probably similar reactions, giving rise to intermediate thiol derivatives, constitute an important factor in the formation of sulphur dyestuffs when *p*-aminophenols and hydroxydiphenylamine derivatives are heated with sodium polysulphide.

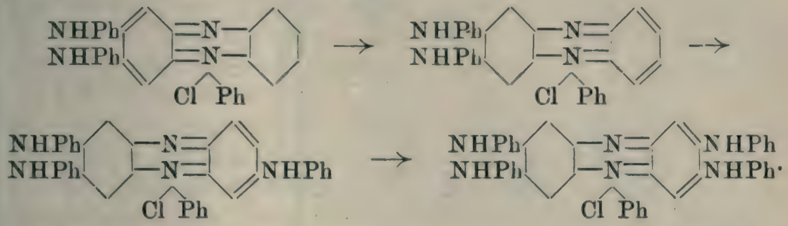
The direct introduction of amino-groups into the nucleus of quinones or quinonoid compounds is known in a large number of cases; thus α- and β-naphthaquinones, when treated with aniline, are converted into their monoanilino-derivatives, $C_{10}H_5O_2{\cdot}NHPh$, whilst *p*-benzoquinone gives dianilino-*p*-benzoquinone and its anilides. Anilino-derivatives of *p*-benzoquinone and of *p*-benzoquinoneanilides are also produced when aniline is subjected to oxidation under neutral or very feebly acid conditions (compare Willstätter and Majima, *Ber.*, 1910, **43**, 2588; Majima, *Ber.*, 1911, **44**, 229, 3080). These compounds constitute the intermediate stages in the formation of indulines and nigrosines, in which cases the rôle of oxidising agent is fulfilled by the aminoazobenzene or nitrobenzene respectively. Assuming as before that the primary oxidation product of aniline is again the yellow imide of Caro, we may picture the further condensation to occur by alternate addition and reoxidation in the following manner:



All these compounds give rise to indulines on heating with aniline and aniline hydrochloride, the closing of the phenazonium ring being attributable to direct quinonoid addition, in which the amine residue taking part in the reaction is a portion of the quinonoid molecule itself:



By the transference of the quinonoid bonds to the other ring, an occurrence which has been specially studied by Kehrmann (*Ber.*, 1898, **31**, 977), this ring also becomes capable of indirect addition, and thus a further introduction of amine residues is effected, and bluer shades of induline are produced:



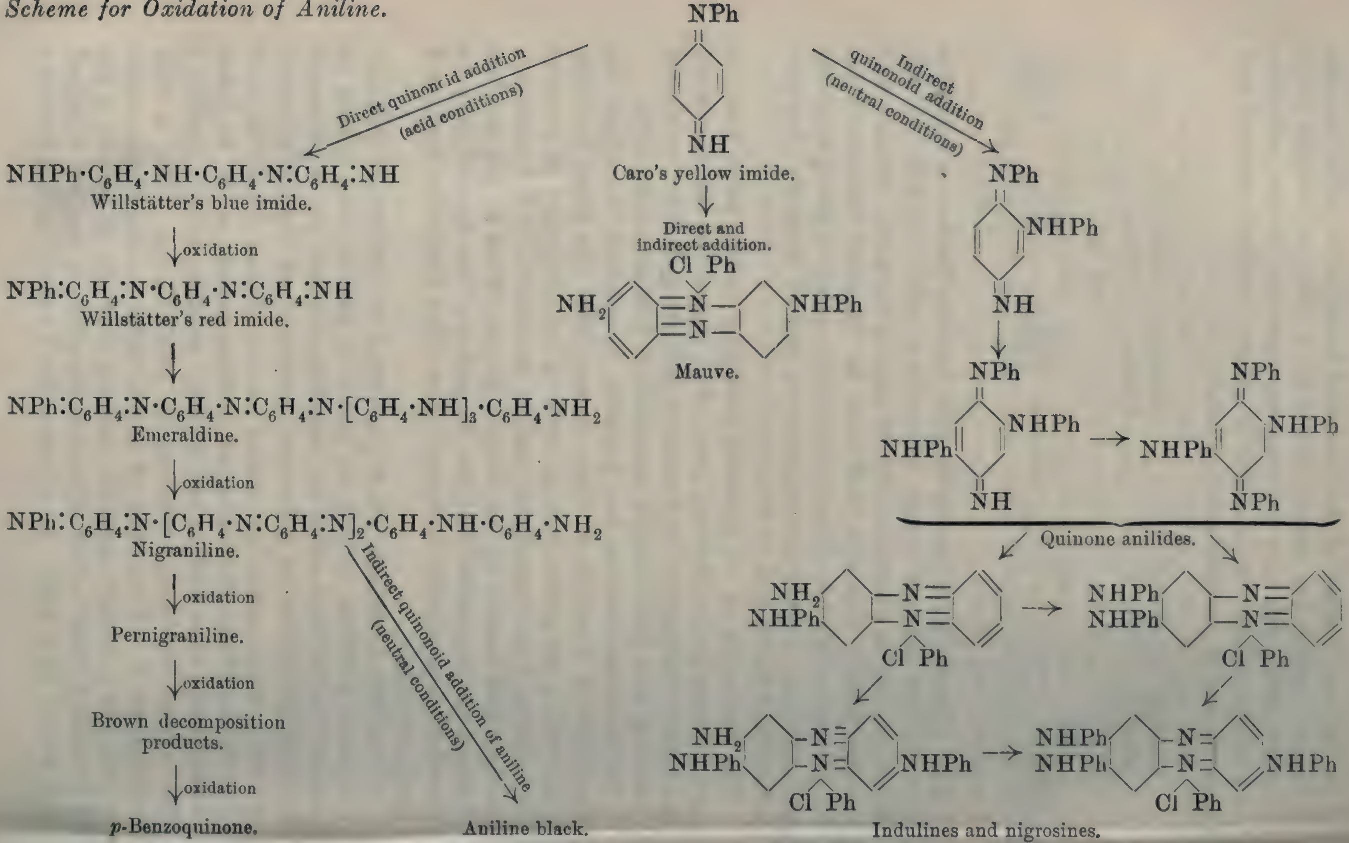
The introduction of amine residues into the benzene or naphthalene nucleus brought about by indirect quinonoid addition has been observed in a large number of cases in the azine, thiazine, and oxazine series. Amongst them may be instanced the convertion of phenylphenazonium chloride into *apo*safranine, of phenylnaphthaphenazonium chloride into rosinduline, and of Meldola's blue into substituted derivatives of Nile-blue.

The formation of all dyestuffs belonging to the azine, oxazine, and thiazine series, starting from their respective raw materials, are readily represented by a series of indirect and direct quinonoid additions with intermediate reoxidations (compare Bucherer).

Similar considerations can probably be applied to explain the formation of dyestuffs of other classes; thus the great tendency exhibited in the anthraquinone series to the production of complex ring systems (vat dyestuffs) is possibly attributable to the attraction for hydrogen exerted by the ketonic groups. Even in the azo-class it seems not impossible that the formation of the dyestuff may be preceded by an unstable quinonoid form of the diazonium compound (compare Cain).

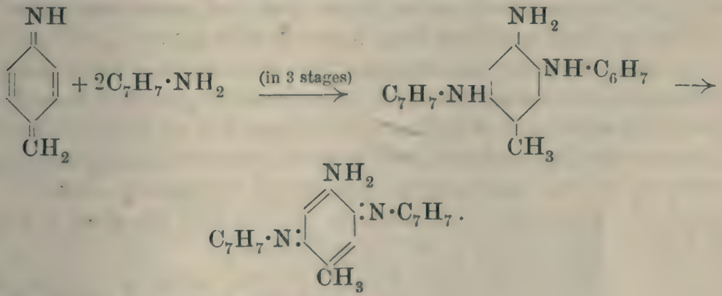
As to the conditions which predispose to direct or indirect quinonoid addition, it may be noted in general with regard to amines, that whilst strongly acid conditions favour direct quinonoid addition (formation of indamines, formation of triphenylmethane dyestuffs, etc.), neutral or weakly acid conditions favour indirect quinonoid addition (formation of anilinoquinones, etc.). In other words, amine salts tend to add *directly*, reacting as $H(C_6H_4{\cdot}NH_2)$; free amines *indirectly*, reacting as $H(NH{\cdot}C_6H_5)$. This is well brought out in the oxidation of aniline under various circumstances in which it is clearly apparent that the condition of acidity is the determining factor which regulates the ultimate product obtained (see scheme on p. 932). In all cases Caro's yellow imide is probably

*Scheme for Oxidation of Aniline.*

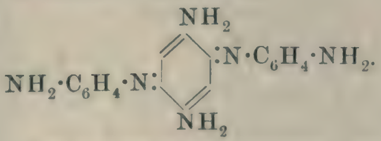

NPh
NH
Caro's yellow imide.
Direct quinonoid addition
(acid conditions)
Indirect quinonoid addition
(neutral conditions)
$NHPh\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot N{:}C_6H_4{:}NH$
Willstätter's blue imide.
oxidation
$NPh{:}C_6H_4{:}N\cdot C_6H_4\cdot N{:}C_6H_4{:}NH$
Willstätter's red imide.
$NPh{:}C_6H_4{:}N\cdot C_6H_4\cdot N{:}C_6H_4{:}N\cdot[C_6H_4\cdot NH]_3\cdot C_6H_4\cdot NH_2$
Emeraldine.
oxidation
$NPh{:}C_6H_4{:}N\cdot[C_6H_4\cdot N{:}C_6H_4{:}N]_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NH_2$
Nigraniline.
oxidation
Pernigraniline.
oxidation
Brown decomposition products.
oxidation
p-Benzoquinone.
Indirect quinonoid addition of aniline
(neutral conditions)
Aniline black.
Direct and indirect addition.
Cl Ph
$NH_2$
NHPh
Mauve.
NPh
NHPh
NH
NPh
NHPh
NHPh
NH
NPh
NHPh
NHPh
NPh
Quinone anilides.
$NH_2$
NHPh
N
N
Cl Ph
NHPh
NHPh
N
N
Cl Ph
$NH_2$
NHPh
N
N
NHPh
Cl Ph
NHPh
NHPh
N
N
NHPh
Cl Ph
Indulines and nigrosines.

the first product of the reaction, but whilst in acid solution this undergoes direct quinonoid addition, with itself finally giving emeraldine and nigraniline, in neutral solution it suffers indirect addition with aniline, giving rise to various anilino-quinones, which on heating with aniline hydrochloride eventually produce indulines. That the condition of acidity is the determining factor in directing the course of these reactions in one direction or the other is clearly shown by the following simple experiment. If to an alkaline aqueous solution of the yellow imide containing aniline in excess there is added concentrated hydrochloric acid, a blue precipitate of Willstätter's imide is immediately formed. If, on the other hand, a small quantity of dilute hydrochloric acid is first added, a reddish-brown precipitate of an anilino-quinone is produced, which is not further altered by adding concentrated hydrochloric acid a few seconds later.

Exactly analogous to the course of the oxidation of aniline in neutral solution is that of *p*-toluidine and of *p*-phenylenediamine. The former gives Barsilowsky's base, the formation of which probably occurs as follows (Green, T., 1893, **63**, 1395):



The production of Bandrowski's base,



from *p*-phenylenediamine may be attributed to an analogous reaction starting from quinonedi-imide.

This paper was communicated to the Eighth International Congress of Applied Chemistry, New York, 1912.

Department of Tinctorial Chemistry,
The University, Leeds.

# XCVI.—*Influence of Increase of Initial Temperature on the Explosiveness of Gaseous Mixtures.*

By ALBERT PARKER, B.Sc.

MANY experiments have been carried out by various investigators to determine the lower limits of explosion of combustible gases, such as hydrogen, carbon monoxide, and methane, but these limits are not yet known with any great degree of accuracy, except in the case of methane. This variation in the results obtained is to be explained by the influence of such conditions as size and shape of the containing vessel and the nature and position of the firing agent employed.

Roszkowski (*Zeitsch. physikal. Chem.*, 1891, **7**, 485) found that mixtures containing a smaller percentage of combustible gas could be fired in a sphere-shaped vessel better than in a narrow tube. It is also well known that a gaseous mixture contained in a vertical tube is more easily fired by sparking at the bottom than at the top. Roszkowski carried out many experiments on the influence of initial temperature on explosion limits of gases, but since that time very little work has been done on this point.

In the following experiments no attempt has been made to determine the lower limits of a combustible gas at different temperatures when mixed with air or oxygen, but an attempt has been made to obtain a mixture which would not completely explode by sparking at one temperature, and would completely explode when sparked at some other temperature. In this way the effect of change of initial temperature could be ascertained.

Experiments were made with hydrogen, methane, carbon monoxide, and coal gas. The gaseous mixtures were made by mixing measured volumes of the constituent gases in a glass gasometer containing water; consequently, the mixtures were saturated with water-vapour at from 15° to 18°. The gasometer held about 15 litres, which was sufficient to allow many experiments to be made at the ordinary temperature and at 100°. This was essential, as it is very difficult to obtain two mixtures of identical composition, especially when dealing with coal gas mixtures.

The gaseous mixtures were made by first making a mixture of a certain known composition, and then altering it by addition of one or other of the constituent gases until the required mixture was obtained; for example, in the case of mixtures of methane and oxygen, a mixture containing 6·35 per cent. of methane was first made. This was found to explode completely at the ordinary temperature. A calculated quantity of oxygen was then added, so that the gas contained 6·3 per cent. of methane. A further quantity of oxygen was added, altering the composition to 6·25 per cent. of methane, which was found to be the required mixture.

*Apparatus.*—The apparatus consisted of a graduated explosion pipette of 100 c.c. capacity. The sparking platinum points were near to the top, so that the volume above the platinum points was only 1 c.c. A three-way tap allowed the pipette either to be opened to the air or connected to the gasometer containing the mixture to be examined. The pipette was surrounded by a wide glass tube, through which steam could be passed. The volume and pressure of the gas to be fired were controlled by means of a mercury reservoir. A break spark of constant strength was used to fire the gases, and was obtained from a Ruhmkorff coil by screwing the coil up and rapidly breaking the contact by means of the switch. The gas was measured under atmospheric pressure before and after sparking, and the amount of gas burned was calculated from the observed contraction.

Experiments were conducted with the various gaseous mixtures at the ordinary temperature, and at three different pressures. At 100° experiments were made at (1) atmospheric pressure, (2) a pressure equal to that which would have been obtained by heating the gas from the ordinary temperature to 100° at constant volume, and (3) a still higher pressure. In this way the effects of pressure change could also be observed. The progress of the flames produced on sparking was followed after previously darkening the room.

### *Experiments with Hydrogen.*

For these experiments mixtures of hydrogen with oxygen and with air were used. The hydrogen was prepared from pure zinc and sulphuric acid, and was freed from hydrocarbons by passing through hot potassium permanganate solution. The oxygen was prepared from manganese dioxide and potassium chlorate, and was freed from chlorine by means of sodium hydroxide solution. The results obtained for hydrogen mixtures are given in the following tables. Each result represents the mean value of several experiments.

TABLE I.

Hydrogen = 8·4, oxygen = 91·6 per cent.

| Temperature. | Pressure in mm. | Amount burned. Per cent. | Observations. |
|---|---|---|---|
| 17° | 763 | 0·57 | Flame only travelled a short distance down the burette. |
| 17 | 1056 | 0·7 | |
| 17 | 1342 | 0·76 | |
| 100 | 763 | 0·89 | |
| 100 | 970 | 1·1 | |
| 100 | 1361 | 1·3 | |

The above results showing the percentage of hydrogen burned are calculated on the total volume of the mixture used.

### TABLE II.

Hydrogen = 8·7, oxygen = 91·3 per cent.

| Temperature. | Pressure in mm. | Amount burned. Per cent. | Observations. |
|---|---|---|---|
| 17° | 766 | 1·3 | Flame part way |
| 17 | 1011 | 1·9 | ,, ,, ,, |
| 17 | 1011 | 7·3 | ,, throughout |
| 17 | 1335 | 1·9 | ,, part way |
| 100 | 766 | 1·8 | ,, ,, ,, |
| 100 | 971 | 2·1 | ,, ,, ,, |
| 100 | 971 | 8·6 | ,, throughout |
| 100 | 1384 | 5·3 | ,, part way |
| 100 | 1384 | 8·65 | ,, throughout |

### TABLE III.

Hydrogen = 8·7, air = 91·3 per cent.

| Temperature. | Pressure in mm. | Amount burned. Per cent. | Observations. |
|---|---|---|---|
| 17° | 754 | 1·14 | Flame part way |
| 17 | 974 | 1·36 | |
| 17 | 1337 | 1·7 | |
| 100 | 754 | 1·85 | ,, ,, ,, |
| 100 | 754 | 8·45 | ,, throughout |
| 100 | 960 | 2·1 | ,, part way |
| 100 | 960 | 8·48 | ,, throughout |
| 100 | 1378 | 3·1 | ,, part way |
| 100 | 1378 | 8·42 | ,, throughout |

In some cases in the above results two values are given for the percentage of hydrogen burned under the same conditions of temperature and pressure. This is to show that sometimes on sparking the flame travelled only a short disatance, and at other times the flame travelled throughout the mixture. The lower value given is the mean of the results obtained from the experiments in which the flame travelled only a short distance, and the higher value is the mean of those experiments in which the flame travelled throughout.

From the foregoing results for hydrogen mixtures it may be concluded:

(1) When a mixture of hydrogen with oxygen or with air below the lower limit is sparked at an initial temperature of 17° or 100°, increase of initial pressure from one to two atmospheres causes an increase in the amount of hydrogen burned.

(2) Rise of initial temperature increases the amount of hydrogen burned.

(3) Even in those experiments in which the flame has travelled throughout the gas, the combustion of hydrogen is incomplete, and it is more incomplete at the ordinary temperature than at 100°.

(4) It is possible to obtain a mixture of hydrogen with oxygen or with air which will not explode at the ordinary temperature and pressure, but which will explode when heated to 100° at either constant pressure or constant volume.

### *Experiments with Carbon Monoxide.*

The carbon monoxide was prepared from sodium formate and sulphuric acid, and was purified from carbon dioxide by means of potassium hydroxide solution. Analysis of the gas showed it to contain 99·8 per cent. of carbon monoxide.

TABLE IV.

Carbon monoxide = 14·5, air = 85·5 per cent.

| Temperature. | Pressure in mm. | Amount burned Per cent. | Observations. |
|---|---|---|---|
| 15° | 771 | 0·57 | Flame part way |
| 15 | 1018 | 0·71 | |
| 15 | 1331 | 0·86 | |
| 100 | 771 | 14·3 | Flame throughout |
| 100 | 981 | 14·5 | |
| 100 | 1379 | 14·5 | |

TABLE V.

Carbon monoxide = 15·7, oxygen = 84·3 per cent.

| Temperature. | Pressure in mm. | Amount burned. Per cent. | Observations. |
|---|---|---|---|
| 15° | 755 | 0·86 | Flame part way |
| 15 | 987 | 1·72 | |
| 15 | 1297 | 2·0 | |
| 100 | 755 | 15·6 | Flame throughout |
| 100 | 961 | 15·7 | |
| 100 | 1337 | 15·65 | |

From the results for carbon monoxide mixtures it may be concluded that:

(1) Increase of initial pressure increases the amount of carbon monoxide burned.

(2) Increase of initial temperature increases the amount of carbon monoxide burned.

(3) It is possible to obtain a mixture of carbon monoxide with air or oxygen which will not completely explode at the ordinary temperature and pressure, but which will completely explode after heating to 100° at either constant pressure or constant volume.

(4) It was also found that a 15 per cent. mixture of carbon monoxide and air completely exploded when sparked at the ordinary temperature and pressure, whereas a 15 per cent. mixture of carbon monoxide and oxygen did not completely explode under the same conditions.

### *Experiments with Methane.*

The methane was prepared by the action of hot water on pure previously fused aluminium carbide. The evolved gas was purified by passing through an ammoniacal solution of cuprous chloride to remove acetylene, and then through dilute sulphuric acid to remove ammonia. The gas thus prepared was carefully analysed, the hydrogen present being estimated by mixing with oxygen and passing the mixture over palladium-black. Rather more than the calculated quantity of oxygen was added, and the mixture dried by passing through sulphuric acid. The dry gas was passed over palladium-black at 100°, and then through alkaline pyrogallate solution to remove oxygen. Analysis showed the gas to only contain a small quantity of nitrogen as impurity.

TABLE VI.

Methane = 6·0, air = 94·0 per cent.

| Temperature. | Pressure in mm. | Amount burned. Per cent. | Observations. |
|---|---|---|---|
| 16° | 755 | 0·56 | Flame part way |
| 16 | 988 | 0·71 | |
| 16 | 1297 | 0·86 | |
| 100 | 755 | 6·0 | Flame throughout |
| 100 | 961 | 5·9 | |
| 100 | 1337 | 6·0 | |

TABLE VII.

Methane = 6·25, oxygen = 93·75 per cent.

| Temperature. | Pressure in mm. | Amount burned. Per cent. | Observations. |
|---|---|---|---|
| 16° | 768 | 0·86 | Flame part way |
| 16 | 1000 | 1·0 | |
| 16 | 1312 | 1·15 | |
| 100 | 768 | 6·30 | Flame throughout |
| 100 | 974 | 6·20 | |
| 100 | 1337 | 6·25 | |

From the above results for methane mixtures it may be concluded that:

(1) Increase of initial temperature or pressure causes an increase in the amount of methane burned.

(2) It is possible to obtain a mixture of methane with air or oxygen which will not completely explode when sparked at the ordinary temperature and pressure, but which will completely explode when sparked after heating to 100° at either constant pressure or constant volume.

(3) It was also found that a 6·2 per cent. mixture of methane and air completely exploded when sparked at the ordinary temperature and pressure, whereas a 6·2 per cent. mixture of methane and oxygen did not completely explode under the same conditions.

### *Experiments with Coal Gas.*

In the experiments with coal gas mixtures the same sample of gas was not used for oxygen as for air mixtures, so that probably the composition of the coal gas differed slightly in the two series.

### TABLE VIII.

Coal gas = 9·4, oxygen = 90·6 per cent.

| Temperature. | Pressure in mm. | Amount burned. Per cent. | Observations. |
|---|---|---|---|
| 17° | 764 | 1·87 | Flame part way |
| 17 | 1038 | 2·07 | |
| 17 | 1341 | 2·23 | |
| 100 | 764 | 3·0 | ,, ,, ,, |
| 100 | 764 | 9·4 | ,, throughout |
| 100 | 971 | 3·1 | ,, part way |
| 100 | 971 | 9·2 | ,, throughout |
| 100 | 1391 | 2·9 | ,, part way |
| 100 | 1391 | 9·2 | ,, throughout |

### TABLE IX.

Coal gas = 8·55, air = 91·45 per cent.

| Temperature. | Pressure in mm. | Amount burned. Per cent. | Observations. |
|---|---|---|---|
| 17° | 752 | 1·2 | Flame part way |
| 17 | 1034 | 1·7 | |
| 17 | 1336 | 2·2 | |
| 100 | 752 | 8·3 | ,, throughout |
| 100 | 957 | 8·5 | |
| 100 | 1380 | 8·5 | |

In order to be able to calculate the amount of coal gas burned from the observed contraction in volume, it was first necessary to make a richer mixture of coal gas and air of known composition, and observe the contraction in volume after sparking at the ordinary temperature and at 100°. The results obtained for coal gas mixtures are very similar to those which were obtained for hydrogen, carbon monoxide, and methane.

### *General Conclusions.*

(1) Increase of initial temperature of gaseous mixtures of hydrogen, carbon monoxide, methane, or coal gas with air or oxygen causes an increase in the explosiveness of such mixtures; that is to say, the values of the lower limits of such gases are lowered. This is the effect to be expected, since when the temperature is raised the mixture is brought nearer to its ignition-temperature, and the cooling effect produced by the walls of the containing vessel is decreased.

(2) The effect of increase of initial temperature is much less in the case of hydrogen mixtures than with methane or carbon monoxide mixtures.

(3) Increase of initial pressure also increases the explosiveness of the above gaseous mixtures.

(4) The lower limit of hydrogen is approximately the same when mixed with air as when mixed with oxygen, but the values of the lower limits of carbon monoxide, methane, and coal gas are higher for oxygen mixtures than for air mixtures.

I wish to express my indebtedness to Prof. Dixon for much valuable advice during the course of this work.

UNIVERSITY OF MANCHESTER.

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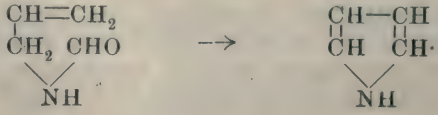
## XCVII.—*Allylamine Derivatives.*

By WILHELM GLUUD, Ph.D.

THE production of pyrrole from allyl derivatives has been described by Königs (*Ber.*, 1879, **12**, 2344), who passed ethylallylamine over lead oxide at 400—500°. Since then no progress has been effected in this method of preparing pyrrole, and the description of the following compounds may therefore be of interest. The reaction and its application to similar substances will be dealt with in another communication.

The simplest acyl derivative of allylamine is allylformamide, the empirical formula of which differs from that of pyrrole only by one molecule of water:



It seems, however, to have only a slight tendency to pass into pyrrole derivatives, although these can be obtained by heating allylformamide to 260°, but the yield was so small that the reaction did not repay further investigation. The high temperature caused the formation of many decomposition products, including carbon monoxide and ammonium carbonate. Dehydrating agents gave no better results.

Allylthiocarbimide on heating with sodium in a sealed tube gave compounds which showed the pyrrole reaction with pine-wood quite distinctly, and a similar result was obtained by passing the vapour of the compound over heated copper, but in both cases the yield was very small owing to the violent character of the reaction. It is a remarkable fact, however, that small quantities of pyrrole compounds are formed during the preparation of allylformamide from allylthiocarbimide and formic acid.

It occurred to me that better results might be obtained by using allyloxamic acid, an expectation which has been satisfactorily confirmed, as this substance was found to be an excellent material for the production of pyrrole derivatives. For this purpose it was necessary to find an easy way of preparing it. An attempt was made to obtain it by a method analogous to that used by Clayton (*Ber.*, 1895, **28**, 1666) in the preparation of allylformamide, namely, from oxalic acid and allylthiocarbimide, but the products of the reaction are complicated and difficult to separate, being for the most part allylamine oxalates, besides the allylamine salt of allyloxamic acid, and some compounds containing sulphur. The latter were not investigated, as they were of no use for the purpose of this research, but possibly they may be of interest as intermediate products, as they readily evolve carbonyl sulphide, and may therefore be assumed to contain this substance only loosely combined. A better method was to prepare the ethyl ester of allyloxamic acid from allylamine and ethyl oxalate, and then to hydrolyse the ester.

## EXPERIMENTAL.

### *Allylformamide*, $CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CHO$.

This substance was previously prepared by Clayton (*Ber.*, 1895, **28**, 1666), but as no details of the yield are given, some improvements may be noted which ensure a rapid preparation of any quantity of the compound. If anhydrous formic acid is used, the reaction takes much less time, and can be carried out on a water-bath, and the oil need not be distilled under diminished pressure.

Allylthiocarbimide (102 grams) and anhydrous formic acid (53 grams) are heated under reflux on the water-bath, the condenser being connected to a gas wash-bottle filled with water. The evolution of gas begins at once, but after about an hour the reaction suddenly becomes violent, and should be moderated by slightly lowering the temperature. When the liquid stops boiling the reaction is completed by heating for half an hour on the water-bath. The liquid is then distilled; much carbonyl sulphide is evolved below 190°, and the allylformamide passes over at 213—218°, the yield being about 70 per cent. of the theoretical. The residue in the flask gave the pyrrole reaction with pine-wood. In another experiment, from 150 grams of allylthiocarbimide 91 grams of allylformamide were obtained, which boiled at 215—216°. It is an oily liquid with an unpleasant odour, readily soluble in water, ether, or alcohol. When prepared in this way, it is pure enough for most purposes, but can be purified by extraction with light petroleum or by redistillation over charcoal; the compound then still contains traces of sulphur.

If allylformamide, however, is distilled over phosphoric oxide or zinc chloride, a small quantity of oil passes over about 120—140°. This oil is lighter than water, and does not mix with it; it gives the pyrrole reaction distinctly. On heating allylformamide in a sealed tube for several hours, decomposition begins about 260°. There is a high pressure in the tubes, due to carbon monoxide, and a small quantity of a pyrrole derivative of high boiling point is formed, along with resinous products and ammonium carbonate. Similar results were obtained when allylacetamide was used.

*Diallyloxamide*, $CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH{:}CH_2$.

This compound was prepared by Wallach and Stricker (*Ber.*, 1880, **13**, 513), but no accurate description of the preparation, properties, or details of analysis are given in their paper. Allylamine (3·8 grams) dissolved in 25 c.c. of ether is mixed with freshly distilled ethyl oxalate (3·5 grams) dissolved in 25 c.c. of ether, and the mixture cooled to 0°. After several hours the crystals formed (3·5 grams) are collected and recrystallised from acetone. Analysis of the compound, dried in a desiccator, showed that it was quite pure, the yield being about 87 per cent. of the theoretical:

0·1631 gave 0·3412 $CO_2$ and 0·1020 $H_2O$. C=57·05; H=7·00.
0·1700 „ 23·8 c.c. $N_2$ at 16° and 768 mm. N=16·54.
$C_8H_{12}O_2N_2$ requires C=57·10; H=7·19; N=16·67 per cent.

The compound crystallises in long, narrow plates, fairly soluble in hot alcohol, chloroform, benzene, and excess of hot water or ether. It is readily soluble in warm dilute acetic acid, and addition of calcium chloride and sodium acetate to the solution produces no precipitation of oxalate even on boiling for a short time.

The aqueous solution rapidly decolorises bromine water. When boiled with alkalis, allylamine is evolved.

### *Allyloxamic Acid*, $CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CO_2H$.

In order to obtain this compound, it is first necessary to prepare the *ethyl* ester, $CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CO_2Et$. This is done by mixing 100 grams of ethyl oxalate in 100 c.c. of ether with 37 grams of allylamine in 60 c.c. of ether and cooling to 0°. After an hour, the ether is evaporated off, and the residue which contains crystals is shaken with light petroleum. The solid remains suspended in the ether, and the ethyl allyloxamate which forms the lower layer is easily separated. On distillation, a small fraction passes over below 100°, then the temperature rises rapidly, and at 252° the ester (66 grams) distils over, the yield being 65 per cent. of the theoretical. It still, however, contains a small quantity of diallyloxamide, which partly separates on cooling. If the whole is hydrolysed this impurity can be completely removed.

The ester is a pale yellow liquid with an unpleasant, garlic odour. It is heavier than water, and readily soluble in the usual organic solvents or in excess of hot water, from which it separates on cooling. The aqueous solution decolorises bromine-water immediately.

In the following experiments it was unnecessary to use the pure product. The ester (2·3 grams) is shaken with 15 c.c. of *N*-sodium hydroxide until, after half an hour, the garlic odour has disappeared. Then 15 c.c. of *N*-hydrochloric acid are added, when crystals of diallyloxamide separate out. These are collected, and the filtrate is evaporated to dryness. The residue is extracted with ether and the solution evaporated, leaving a syrupy mass, which, on mixing with light petroleum, soon becomes crystalline (1·3 grams). The crystals can be purified by recrystallisation from a very small quantity of benzene and then from chloroform, from which allyloxamic acid (0·85 gram) separates in silky, square plates, which melt at 97—98°, forming a colourless liquid. They are very soluble in water, alcohol, or acetone, readily so in ether, hot chloroform or benzene, and sparingly soluble in hot light petroleum. From the last three solvents the substance crystallises on cooling the solution. The aqueous solution decolorises bromine-water at once. The substance, after being left in a desiccator, was analysed:

0·2093 gave 0·3563 $CO_2$ and 0·1032 $H_2O$. $C=46·43$; $H=5·52$.
0·2024 „ 18·8 c.c. $N_2$ at 18° and 760 mm. $N=10·86$.
$C_5H_7O_3N$ requires $C=46·49$; $H=5·47$; $N=10·85$ per cent.

The *calcium* salt is prepared by mixing the crude ethyl ester (50 grams) with 160 c.c. of 2*N*-sodium hydroxide and cooling to 0°. When all the oil has disappeared, the liquid is filtered, and a solution of anhydrous calcium chloride (20 grams in 50 c.c. of water) is added to the filtrate. On cooling to 0° the calcium salt separates in crystals, which are collected and dried on a water-bath (40·5 grams), the yield being about 80 per cent. of the theoretical. They can be redissolved in about twenty times their volume of boiling water, and the solution cleared with charcoal. From this solution the salt separates in characteristic, narrow, compact prisms, which acquire a syrupy consistency about 160°. Analysis shows that the air-dried crystals contain two molecules of water:

0·2002 * at 100° over phosphoric acid under 10—12 mm. pressure gave 0·0215 $H_2O$. $H_2O=10·74$.

$C_{10}H_{12}O_6N_2Ca,2H_2O$ requires $H_2O=10·84$ per cent.

0·1787 † gave 0·0340 CaO. Ca=13·60.

$C_{10}H_{12}O_6N_2Ca$ requires Ca=13·53 per cent.

The salt, when heated alone, or with lime, or equivalent substances, easily yields a yellow oil, which does not mix with water, resinifies with acids, and gives the pyrrole reaction.

The *potassium* salt is prepared by boiling the aqueous solution of the calcium salt for some minutes with the required quantity of anhydrous potassium hydroxide. The solution is filtered and evaporated on a water-bath, leaving a waxy mass. This is mixed with alcohol, and becomes instantly solid. One gram of this solid is dissolved in a mixture of 20 c.c. of alcohol and 0·5 c.c. of water, from which solution 0·7 gram of the salt crystallises in thin plates. The air-dried salt contains no water of crystallisation, as it loses practically no weight when dried at 100° over phosphoric acid at 10—12 mm. pressure. When heated to 230° it forms a syrupy liquid, which decomposes at a higher temperature, giving oily distillates, which contain pyrrole derivatives.

### *Action of Oxalic Acid on Allylthiocarbimide.*

Crystallised oxalic acid (30 grams) and allylthiocarbimide (30 grams) were heated under reflux for five hours at 125°. The action was not then complete, as the evolution of gas still continued. The product, which solidified on cooling, was washed with light petroleum to remove any unchanged allylthiocarbimide, and 23 grams were crystallised from alcohol, from which transparent prisms separated, melting at 135—136°, readily soluble in hot water or alcohol, but practically insoluble in most organic solvents. It was dried in a vacuum desiccator, and then analysed:

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* Air dried.

† Anhydrous.

0·1943 gave 0·2905 $CO_2$ and 0·1105 $H_2O$. C=40·78; H=6·36.

$C_5H_9O_4N$ requires C=40·80; H=6·17 per cent.

The product is therefore *allylamine hydrogen oxalate.* When heated above its melting point much gas is evolved, and a colourless residue left, which does not give the pyrrole reaction. It can also be prepared by mixing 1·2 grams of allylamine with a solution of 2 grams of oxalic acid in alcohol or acetone in the cold.

In another experiment a mixture of allylthiocarbimide (52 c.c.) and crystallised oxalic acid (77 grams) was heated on a water-bath for about twenty-five hours until no further evolution of gas was observed, and the odour of allylthiocarbimide had disappeared. The product was a clear liquid, which on cooling solidified to a waxy substance, consisting of an oil (24 grams) and a waxy solid (75 grams). The oil was evaporated on a water-bath, and the partly crystalline residue shaken with acetone, when allylamine oxalate (7·5 grams) separated out. The wax-like solid was also shaken with acetone, in which the greater part dissolved, leaving 29 grams of fine crystals melting at 130—134°. (Allylamine hydrogen oxalate melts at 135—136°.) The acetone solution was evaporated in a vacuum, yielding 21 grams of an unpleasant-smelling oil, which solidified on cooling, and appeared to be a mixture of various sulphur compounds, as on heating it gave off much carbonyl sulphide. The production of allylamine oxalate shows that if the reaction is allowed to be completed there is still not sufficient oxalic acid in spite of the excess used.

A mixture of anhydrous oxalic acid (55 grams) and allylthiocarbimide (50 grams) when heated for eighteen hours on a water-bath yielded 55 grams of crystals, more than 60 per cent. of which consisted of allylamine hydrogen oxalate, so that in this experiment also oxamic allyl acid could only have been formed in small quantity.

One experiment may be described, showing the course of this reaction in aqueous solution. Crystallised oxalic acid (70 grams), 50 grams of allylthiocarbimide, and 100 c.c. of water were boiled under reflux for thirty-six hours, the reaction being then complete. The liquid was evaporated on a water-bath until the aqueous layer acquired a syrupy consistency, when it was mixed with twice its volume of alcohol, and the crystals of allylamine oxalate (24 grams) formed were collected. The mother liquor was evaporated to dryness and the residue dissolved in alcohol, when a further separation of the oxalate (6 grams) took place. The filtrate was mixed with ether, and kept in ice for some hours. The crystals then formed (8·5 grams) were removed from the solution, which on evaporation left an oil, which was not further investigated. The crystalline product was recrystallised from a very small quantity of hot chloroform and again from 50 c.c. of acetone; 3 grams of this product were again recrystallised from 75 c.c. of acetone, from which thin, transparent plates (2 grams) separated, melting at 111—112°. These were dried at 100° and analysed:

0·1622 gave 0·3044 $CO_2$ and 0·1091 $H_2O$. C=51·18; H=7·53.
0·1588 „ 19·8 c.c. $N_2$ at 17° and 772 mm. N=14·73.
$C_8H_{14}O_3N_2$ requires C=51·58; H=7·58; N=15·05 per cent.

This compound is *allylamine allyloxamate*,

$$CH_2\colon CH\cdot CH_2\cdot NH\cdot CO\cdot CO_2H,\ NH_2\cdot CH_2\cdot CH\colon CH_2.$$

It can also be prepared from the corresponding calcium salt. One gram of allylamine was added to 3 grams of the calcium salt dissolved in 75 c.c. of hot water, and the calcium precipitated with carbon dioxide. The hot solution was filtered, evaporated in a vacuum, and the residue dissolved in hot acetone. On cooling, 2·4 grams of crystals separated, which were identical with the above allylamine salt. It is extremely soluble in water or hot alcohol, very sparingly so in ether or benzene. The aqueous solution is neutral, decolorises bromine water instantly, and on addition of calcium chloride yields the corresponding very characteristic calcium salt.

*Allylamine oxalate*, as obtained in the above experiment, can be purified by crystallisation from 95 per cent. alcohol. Three grams of the purified product were dissolved in 100 c.c. of hot 97·5 per cent. alcohol, from which solution, on gradually cooling, small, compact prisms separated out on the sides of the flask. The liquid was then decanted and slowly cooled. This product was dried in a vacuum desiccator and analysed:

0·1522 gave 0·2638 $CO_2$ and 0·1027 $H_2O$. C=47·27; H=7·55.
0·1300 „ 15·2 c.c. $N_2$ at 18° and 770 mm. N=13·73.
$C_8H_{16}O_4N_2$ requires C=47·03; H=7·90; N=13·73 per cent.

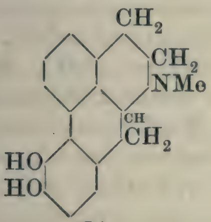
It melts and decomposes at 181°, and is very soluble in water, but practically insoluble in organic solvents. It can also be prepared by mixing 2·5 grams of oxalic acid and 2·5 grams of allylamine in acetone solution at 0°. The crystals formed are collected and recrystallised from 97 per cent. alcohol.

Davy Faraday Laboratory.

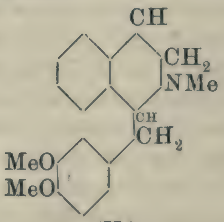
# XCVIII.—*Experiments on the Synthesis of* apo*Morphine.*

### By Francis William Kay and Amé Pictet.

The base, *apo*morphine, $C_{17}H_{17}O_2N$, which, as is well known, forms one of the products obtained by the dehydration of morphine, $C_{17}H_{19}O_3N$, has been studied by a number of investigators, with a view to elucidate its chemical constitution. Amongst these, Pschorr and his pupils must be placed in the first rank, for it is due to their exhaustive investigations (*Ber.*, 1902, **35**, 4377; 1907, **40**, 1984, 1995, 1998) that an insight has been obtained into the constitution of this alkaloid. As a result of their researches, Pschorr and his pupils deduce formula I as the most probable expression of the structure of *apo*morphine:



(I.)

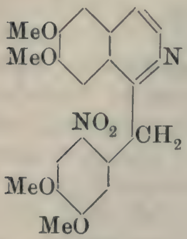


(II.)

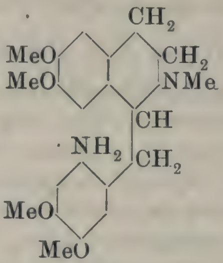
This formula bears a considerable resemblance to that of laudanosine (II), as can be seen on comparing the two.

According to Pschorr, the nucleus in *apo*morphine differs from that in laudanosine only by containing a bond which unites the two benzene rings, and *apo*morphine must thus be considered a derivative of phenanthrene. We have proposed experimentally to verify this hypothesis of Pschorr by attempting a synthesis of *apo*morphine, starting from a compound already containing the nucleus of laudanosine, and then effecting therein the supplementary link in question. Two analogous researches which have already been made and serve as a guide in our present work are due to Pschorr and Gadamer.

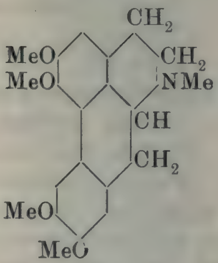
Pschorr (*Ber.*, 1904, **37**, 1926) has attempted to transform papaverine into a derivative of phenanthrene. With this object in view he first proved that the nitropapaverine, obtained by Hesse (*Annalen Suppl.*, 1872, **8**, 292) by treating papaverine with nitric acid, possesses formula III. He prepared its methochloride, and then by reducing the latter with tin and hydrochloric acid, he obtained aminolaudanosine (IV). Apparently, it only remained to diazotise the latter and to treat the product with copper powder, according to the well-known method of Pschorr for synthesising the derivatives of phenanthrene, in order to obtain a phenanthrenolaudanosine (V):



(III.)



(IV.)



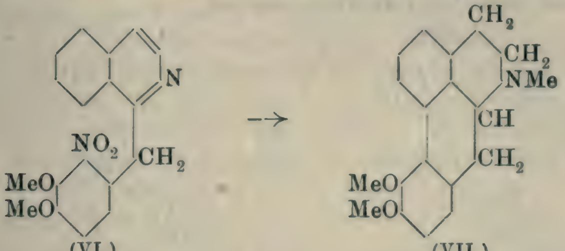
(V.)

Unfortunately, Pschorr was only able to obtain this last base in the form of a non-crystallisable syrup, and to characterise and analyse it in combination with methyl iodide, that is, as the corresponding methiodide, which crystallises in prisms melting at 215°.

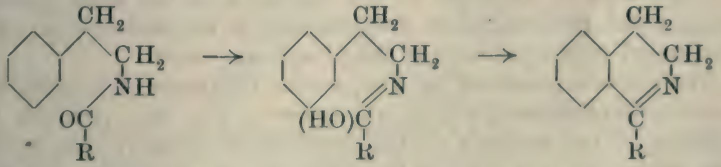
Seven years later Gadamer (*Arch. Pharm.*, 1911, **249**, 680), having repeated this work, showed that the so-called methiodide of phenanthrenolaudanosine, described by Pschorr, was nothing more nor less than the methiodide of racemic laudanosine. The operation of diazotisation, as carried out by Pschorr, had thus merely resulted in eliminating the amino-group of the aminolaudanosine, without closing the phenanthrolic nucleus. By proceeding in a slightly different manner, although still using the same method, Gadamer succeeded in effecting this closure, and obtained in this way the true phenanthrenolaudanosine (V) in the free state and pure (m. p. 137—139°). The latter being inactive to polarised light, whilst from its constitution it should be a racemic substance, Gadamer endeavoured to resolve it into its two optical antipodes. He succeeded in doing so by means of tartaric acid, and was thus able to prove that the dextro-modification (m. p. 119—120°) was identical with glaucine, an alkaloid which has been extracted from *Glaucinum luteum* and *Corydalis cava.* In this way he realised the first synthesis of a natural alkaloid of the phenanthrene series.

A precisely similar process appeared to offer a means of synthesising *apo*morphine, which is very closely related to glaucine from a constitutional point of view. It would suffice as the starting point to take nitroveratryl*iso*quinoline (VI), unknown at present, instead of nitropapaverine (III). By means of the same reactions as used by Pschorr and by Gadamer, it ought to lead to the dimethyl ether of *apo*morphine (VII).

Our first endeavours were directed to preparing this base (VI) or one of its derivatives hydrogenated in the pyridine nucleus. Although the experiments in this direction have proved abortive, the authors consider them sufficiently interesting to justify publication. Of all the methods which have been suggested for building up derivatives of *iso*quinoline, those proposed by the present authors in previous publications (*Ber.*, 1909, **42**, 1973; 1910, **43**, 2384; 1911, **44**, 2030) have the advantage of being comparatively simple, require compounds which are of ready access as the starting point, and give, in addition, remarkably good yields without any harmful by-products. Before commencing the present investigation, we devoted a considerable amount of work to improving and modifying a reaction discovered by Bischler and Napieralski, in such a way as to render it capable of being used in synthesising the *iso*quinoline alkaloids. Briefly stated, our method is as follows. The acyl derivatives of β-phenylethylamine, on boiling with phosphoric oxide in solution in toluene or xylene, lose a molecule of water, and are thereby converted into derivatives of dihydro*iso*quinoline; a reaction which will be readily understood when one writes the substituted amide in its tautomeric enolic form:

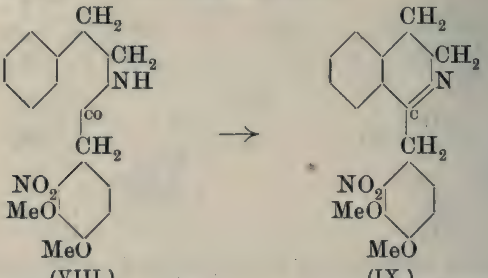


(VI.) (VII.)



A superficial consideration of the formula of the 2-nitro-3:4-dimethoxybenzyl*iso*quinoline, by means of which we had proposed to synthesise dimethyl*apo*morphine, will immediately indicate that we must devise some method of preparing 2-nitrohomoveratroyl-β-phenylethylamine, which, when submitted to dehydration under the conditions mentioned above, would undergo cyclisation with the formation of the dihydro-derivative of the required base; so that, for the moment, the whole problem amounts to the synthesis of 2-*nitrohomoveratric acid* and its condensation with β-phenylethylamine.

Thus far we encountered no great difficulty, but when we came to the conversion of the corresponding amide into the nitroamine, we were astonished to find that, although dehydration had taken place, there was no trace of a basic substance produced, as would be expected from the following reaction:



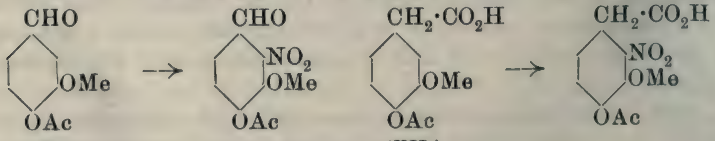
(VIII.) (IX.)

Instead of the latter substance we had obtained an isomeride, derived certainly from 2-nitrohomoveratroyl-β-phenylethylamine by the loss of a molecule of water, but without cyclisation. This dehydro-compound yields, indeed, β-phenylethylamine on reduction and saponification. It is somewhat difficult to make a conjecture as to its constitutional formula. The only one which appears to us to satisfy these conditions, but which it must be admitted is far from proved, is $C_6H_5\cdot CH_2\cdot CH_2\cdot N{:}C{:}CH\cdot C_6H_2(OMe)_2\cdot NO_2$ (X).

The failure to effect this cyclisation of 2-nitrohomoveratroyl-β-phenylethylamine is evidently due to the presence of the nitro-group. It must be recognised, in our opinion, that this group renders the hydrogen atoms of the neighbouring $CH_2$-group much more mobile, and in such a way that it is one of these atoms—and not the atom of hydrogen in the *o*-position in the other benzene ring—which participates in the formation of the molecule of water eliminated in the presence of the phosphoric oxide.

The obstacle presented by the peculiar behaviour of *o*-nitrohomoveratroyl-β-phenylethylamine has arrested, for the moment, the progress of our research on the synthesis of *apo*morphine, but we are continuing the subject by attacking the problem in another direction.

The preparation of the 2-nitrohomoveratric acid required for this synthesis proved to be much more difficult than one would have anticipated. Our first experiments were directed to the nitration of acetylhomovanillic acid, but failed to yield the acid required. Acetylhomovanillic acid (XII) would be expected, from analogy

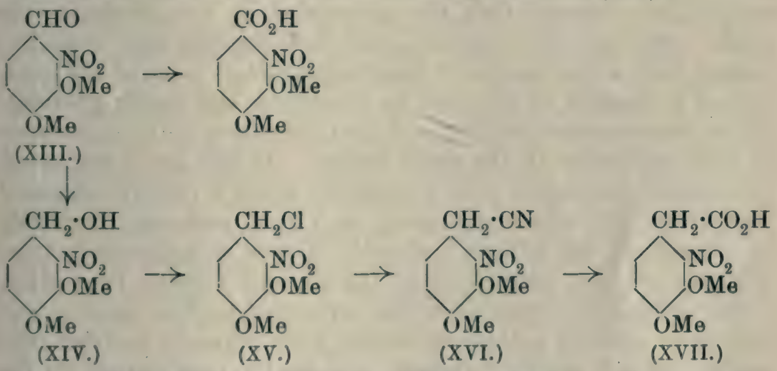


(XI.) (XII.)

to acetylvanillin (XI)—which gives 2-nitrovanillin when treated with nitric acid under suitable conditions—to yield the corresponding 2-nitro-acid when nitrated in the same way:

Despite the most varied experimental conditions, it was found impossible to nitrate acetylhomovanillic acid in such a way as to obtain the 2-nitro-acid, and usually either a dinitro-acid—probably 1:6-dinitrohomovanillic acid—was produced, or the side-chain was oxidised to carboxyl, leading thus to vanillic acid and its nitro-derivatives, which were quite useless for our purpose.

The method which finally proved successful is somewhat indirect, and has as its starting point 2-nitroveratraldehyde (XIII), which was first obtained by Pschorr. On treating this aldehyde with concentrated potassium hydroxide, it undergoes the Cannizzaro reaction, and is transformed into a mixture of 2-nitroveratryl alcohol (XIV) and 2-nitroveratric acid. The succeeding reactions are quite simple, and need only be mentioned very briefly. On treating the nitro-alcohol with phosphorus pentachloride in benzene solution, it is converted into 2-nitroveratryl chloride (XV):



which yields 2-nitrohomoveratronitrile (XVI) on boiling with alcoholic potassium cyanide. The hydrolysis of this nitrile presented considerable difficulty at first, but finally, on applying Pinner's imino-ether method, it was smoothly converted into 2-nitrohomoveratric acid (XVII).

## EXPERIMENTAL.

### *Preparation of 2-Nitroveratryl Alcohol* (XIV) *from the corresponding Aldehyde by Cannizzaro's Reaction.*

This preparation is based on the well-known fact that the aromatic aldehydes undergo a peculiar transformation when they are treated with concentrated alkali hydroxide solution; benzaldehyde, for example, is converted into a mixture of benzyl alcohol and potassium benzoate when shaken with concentrated aqueous potassium hydroxide. Under the same experimental conditions, the nitro-aldehydes behave in precisely the same way, and the reaction, which is a very smooth one, furnishes an excellent yield of the corresponding alcohol and acid. 2-Nitroveratraldehyde, which was prepared in quantity by the method described by Pschorr (*Ber.*, 1899, **32**, 3405), can be applied in the same manner, and is converted with remarkable ease into the required alcohol, 2-nitrovanillic acid being naturally obtained as a by-product at the same time.

To 10 grams of 2-nitroveratraldehyde, which are melted in a strong flask, is added a solution of 10 grams of potassium hydroxide in 10 c.c. of water and 10 c.c. of alcohol, and finally thoroughly mixed by vigorous shaking, and occasionally warmed gently on the water-bath. Shortly after the beginning of the reaction, the potassium salt of 2-nitrovanillic acid begins to separate out in glistening leaflets, and the mixture soon solidifies to a thick paste. After twenty-four hours' treatment, accompanied by vigorous shaking, we assumed that the conversion of the aldehyde into alcohol and acid was complete, and then covered the crystalline magma with a fair amount of ether, extracted as much of the nitro-alcohol as possible by agitating for some time, and finally gradually added, with constant shaking, sufficient anhydrous sodium carbonate to bind practically all the water present. In this way a semi-solid, fine-grained mixture of salts is obtained, which is readily exhausted with ether, five extractions being, as a rule, sufficient completely to remove all the adherent alcohol. Traces of unchanged nitro-aldehyde are now removed from the ethereal solution by washing it once with a concentrated sodium hydrogen sulphite solution and then with aqueous sodium carbonate, after which it is dried over freshly ignited sodium sulphate, and finally fractionated on the water-bath, whilst the last traces of alcohol and ether are removed from the residual oil by connecting the vessel with the vacuum pump. After a short time, the viscid, oily residue solidifies to a hard, crystalline cake, which is then spread on porous earthenware to remove liquid impurities. The dry nitro-alcohol is now dissolved in ether, precipitated with light petroleum, and the oil, which separates, dissolved again in a mixture of light petroleum and ether, whilst the impurities remain behind as a resin. The clear filtrate is now treated while hot with light petroleum until a milkiness begins to form, and then allowed to cool. In this way, 2-*nitroveratryl alcohol* is obtained in slender, yellow needles, which are collected and washed with light petroleum. On allowing the mother liquors to evaporate spontaneously, large, pale yellow, pointed needles are formed. This alcohol was obtained pure by recrystallising once more from the same solvent mixture:

0·1444 gave 0·2694 $CO_2$ and 0·0647 $H_2O$. C = 50·88; H = 5·01.
0·1967 „ 11·7 c.c. $N_2$ at 21° and 731 mm. N = 6·54.
$C_9H_{11}O_5N$ requires C = 50·68; H = 5·21; N = 6·57 per cent.

The nitro-alcohol melts at 68—69°, and dissolves freely in practically all the usual organic solvents, with the exception of light petroleum, in which it is very sparingly soluble even at the boiling point.

### *2-Nitroveratryl Chloride* (XV).

The displacement of the hydroxyl group by chlorine in the alcohol described above is effected by means of phosphorus pentachloride, as the action of hydrogen chloride failed to lead to a satisfactory result.

Two grams of 2-nitroveratryl alcohol are dissolved in 10 c.c. of dry benzene, the solution cooled in ice-water, and gradually treated with 2·1 grams of finely pulverised phosphorus pentachloride, the flask being shaken during the whole of the addition. The phosphorus pentachloride gradually passes into solution, and a little hydrogen chloride is evolved towards the end of the reaction. After remaining for an hour at 0°, the solution, which has meanwhile become paler in colour, is evaporated at 100° in a vacuum in order to remove the phosphoryl chloride, and a viscid, oily residue is obtained, which frequently crystallises directly in the distillation flask, especially if the phosphoryl chloride has been completely removed by dissolving the oil in benzene and evaporating to dryness in a high vacuum. The oily chloride is now dissolved in benzene, filtered, and the clear filtrate diluted with ten times its volume of light petroleum, which causes the precipitation of a little resinous matter—an impurity—which cannot be redissolved by warming the solution. The clear supernatant liquid is decanted hot from the oil, and on cooling deposits a trace of oily impurity, which can be removed by filtration. The filtrate, on complete evaporation on the water-bath, yields a viscid oil, which crystallises to a solid cake on keeping for a short time, especially after being seeded with a crystal of the solid chloride. The somewhat impure solid obtained in this way is purified by solution in a little acetone and slow spontaneous evaporation in the air. The crystalline crusts which form are carefully removed, spread in a thin layer on porous porcelain, and washed with a few drops of acetone. For analysis, the white mass is ground to a fine powder and dried over sulphuric acid in a vacuum desiccator. The yield amounts to practically the original weight:

0·2030 gave 0·1228 AgCl. Cl = 14·96.

$C_9H_{10}O_4NCl$ requires Cl = 15·30 per cent.

2-*Nitroveratryl chloride* melts at 58—59°, and crystallises in yellow, waxy leaflets.

### 2-*Nitrohomoveratronitrile* (XVI).

Potassium cyanide (12 grams) is dissolved in 20 c.c. of boiling water and mixed with a solution of 23 grams of 2-nitroveratryl chloride in 250 c.c. of 96 per cent. alcohol, which precipitates some of the cyanide from solution. The mixture is now heated by immersion in a briskly boiling water-bath, and in the course of about two hours sodium chloride begins to separate out, the amount increasing as the reaction proceeds. In about four to six hours the transformation of the chloride into the nitrile is complete, after which the hot alcoholic solution is poured directly into 1250 c.c. of water, seeded with a crystal of the nitrile, and allowed to remain for some time, which causes the nitrile to separate in yellow, felted needles, along with some resin, which can readily be separated mechanically. The crystalline deposit is collected, spread on a porous plate, and finally dried over sulphuric acid in a vacuum. The yield of crude nitrile amounts to 85 per cent. of the theoretical. The purification of the crude nitrile is best effected by boiling it with 5 litres of water, filtering from undissolved oil, and allowing the clear filtrate to cool slowly, when the nitrile separates out, oily at first, but soon crystallises to a mass of long, hair-like needles, which are slightly coloured, and not quite pure because they melt indefinitely between 60° and 75°. The final purification can best be achieved by dissolving the recrystallised material in 40 volumes of methyl alcohol, and then diluting with hot water until a precipitate begins to form. On cooling, the solution deposits at first an oily suspension, which is removed, whilst the residual nitrile in the clear filtrate separates out only very slowly in the cold, and then quite pure, in slender, colourless needles, which are collected and dried over sulphuric acid in a vacuum desiccator:

0·1462 gave 16·9 c.c. $N_2$ at 21° and 733 mm. N = 12·77.

$C_{10}H_{10}O_4N_2$ requires N = 12·62 per cent.

The nitrile melts at 68—69°, and is readily soluble in the usual organic solvents. It is practically insoluble in cold water, but is appreciably soluble in the hot solvent.

### *Hydrolysis of 2-Nitrohomoveratronitrile: 2-Nitrohomoveratric Acid* (XVII).

Preliminary experiments with potassium hydroxide in aqueous and alcoholic solutions showed that this reagent was entirely unsuited for this saponification, as it only led to the formation of red, uncrystallisable syrups, this being probably due to the presence of the nitro-group. We subsequently found that the nitrile was most conveniently hydrolysed—indirectly, of course—by Pinner's method (*Ber.*, 1883, **16**, 352, 1663; 1884, **17**, 182, 184, 2002; 1892, **25**, 1434; 1895, **28**, 473), an excellent yield of pure acid being readily obtained even from the crude nitrile.

To this end 11 grams (1 mol.) of the nitrile, dissolved in 150 c.c. of absolute ether, are mixed with 8 c.c. (3 mols.) of absolute methyl alcohol, and the solution then saturated at 0° with dry hydrogen chloride. The hydrochloride of the imino-ether frequently separates out of solution during the passage of the hydrogen chloride, and in those cases where it does not, crystallisation usually takes place after a short time, the compound separating in slender, almost colourless needles. The formation of the hydrochloride is complete in a few hours, after which the voluminous, crystalline mass is quickly filtered, washed with dry ether, and finally dried over solid potassium hydroxide in a vacuum desiccator. The yield of imino-ether, starting from crude nitrile, only amounts to 65—75 per cent. of the theoretical, but as only the nitrile can enter into this reaction, whilst the impurities remain dissolved in the ether, this yield is fairly satisfactory, and the method essentially facilitates the preparation of the free acid in a pure state.

The *imino-ether hydrochloride* prepared in this way forms light, colourless needles, which are fairly readily soluble in water, but at the same time it undergoes hydrolytic fission with the formation of ammonium chloride and methyl 2-nitrohomoveratrate, which separates out as an oil.

The direct conversion of the hydrochloride into the free acid is best effected by dissolving it (10 grams) in twenty-five times its weight of water, when a pale yellow, faintly opalescent solution is obtained, which rapidly becomes cloudy owing to the spontaneous separation of the methyl ester. This formation of the methyl ester of the acid is brought to completion by warming the solution for half an hour on the water-bath, after which 40 c.c. of concentrated hydrochloric acid are added, and the boiling continued over a free flame under reflux. In this way the ester which is first formed is saponified and gradually passes into solution in the course of half an hour, whilst complete hydrolysis usually demands two hours. The solution is filtered hot from traces of resin and allowed to cool, when the acid is obtained in large, yellow leaflets, which can be readily purified by recrystallising once from 40 parts of boiling water. For analysis, the substance is dried at 120° until constant in weight, a certain amount of moisture being driven off in the process:

0·1758 gave 0·3204 $CO_2$ and 0·0707 $H_2O$. C=49·71; H=4·5.
0·1804 ,, 10·2 c.c. $N_2$ at 22° and 727 mm. N=6·15.
$C_{10}H_{11}O_6N$ requires C=49·77; H=4·60; N=5·89 per cent.

The pure acid sinters towards 143°, and melts sharply at 146°. It dissolves more or less readily in the common organic solvents, and is very sparingly soluble in cold water, but dissolves appreciably in the hot solvent.

### 2-*Nitrohomoveratroyl-β-phenylethylamine* (VIII).

4·8 Grams (1 mol.) of 2-nitrohomoveratric acid were first converted into the acid chloride in the following manner. The weighed amount of acid is covered with 20 c.c. of chloroform, cooled in water, and gradually treated with 4·2 grams (1·01 mol.) of phosphorus pentachloride in small quantities at a time; the chlorination proceeds somewhat rapidly, and is accompanied by a brisk evolution of hydrogen chloride along with a considerable rise in temperature. As soon as the main reaction is over, the resultant red solution is gently warmed on the water-bath for a short time, that is, until the evolution of hydrogen chloride ceases, and then the phosphoryl chloride is removed as completely as possible by evaporation in a vacuum at a temperature not exceeding 55°. The last traces of phosphoryl chloride, which cling very tenaciously to the residue, can conveniently be removed by dissolving the contents of the distilling flask in dry benzene and repeating the evaporation in a vacuum. In order to facilitate the subsequent coupling with β-phenylethylamine, the residual glassy mass is dissolved in a very small quantity of dry benzene, and this solution is then added in small portions, and alternately with 6 c.c. of 20 per cent. aqueous sodium hydroxide (1·5 mol.) to 2·4 grams (1 mol.) of β-phenylethylamine suspended in 10 c.c. of water, the whole being well cooled in a freezing mixture and continuously shaken. As soon as the whole of the chloride is consumed, the amide which is formed is dissolved in 50 c.c. of benzene, washed with a little water, and finally with dilute acid. The dried benzene solution is submitted to fractional precipitation with light petroleum. The first precipitate obtained contains principally resinous impurities, and is rejected. The clear liquid filtered from it, when treated hot with light petroleum until a precipitate begins to form, and then allowed to cool slowly, yields first an oil, but this soon crystallises in aggregates of pointed prisms, which are collected, the filtrate being subsequently treated in a similar manner.

A third crystallisation is difficult to obtain an account of the solubility of the amide in a large volume of light petroleum, and in this case it is advisable to evaporate the solution to dryness and crystallise the residual resin from a mixture of benzene and light petroleum. By recrystallising the product once more from the same solvent-mixture, it is obtained pure for analysis in almost colourless, thick prisms, which are finally dried over sulphuric acid in a vacuum desiccator:

0·1616 gave 0·3709 $CO_2$ and 0·0855 $H_2O$. C = 62·6; H = 5·92.
0·2260 „ 16·4 c.c. $N_2$ at 19° and 720 mm. N = 7·93.
$C_{18}H_{20}O_5N_2$ requires C = 62·75; H = 5·87; N = 8·14 per cent.

The melting point of *2-nitrohomoveratroyl-β-phenylethylamine* lies at about 86°, with slight previous softening. By recrystallising from hot toluene, the melting point rises to 98°.

### *Attempted Cyclisation of 2-Nitrohomoveratroyl-β-phenylethylamine.*

With the object of bringing about the cyclisation of 2-nitrohomoveratroyl-β-phenylethylamine to form nitroveratryldihydro*iso*quinoline, according to the scheme (VIII—IX) given on p. 950, we operated according to the method indicated above, and heated the first of these two substances with an excess of phosphoric oxide in solution in toluene. Here we found, however, contrary to all our preceding experience, that the elimination of water is slow and difficult. It is no longer sufficient to heat to boiling for three to five minutes only to produce the dehydro-compound; the heating must be continued for fifteen or thirty minutes, and even then the reaction is still incomplete. After shaking the product with water, we proved that the aqueous layer did not contain the least trace of a basic substance, and failed to give a precipitate with sodium carbonate. The whole of the product remains in solution in the toluene layer, which yields a yellow-coloured residue on evaporation to dryness. The major portion of the latter consists of the original substance, unchanged. By recrystallisation from toluene, we succeeded, nevertheless, in isolating a new substance from the yellow residue, which it contains to the extent of 20 to 30 per cent., and to which the yellow coloration is due. This yellow compound clearly constitutes the product of dehydration, for its analysis certainly leads to the formula $C_{18}H_{18}O_4N_2$, which contains one molecule of water less than the original 2-nitrohomoveratroyl-β-phenylethylamine:

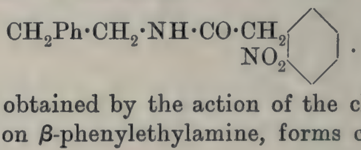
0·1132 gave 0·2749 $CO_2$ and 0·0516 $H_2O$. C = 66·23; H = 5·10.
0·0860 „ 7·0 c.c. $N_2$ at 20° and 717 mm. N = 8·81.
$C_{18}H_{18}O_4N_2$ requires C = 66·22; H = 5·58; N = 8·58 per cent.

This compound separated from boiling toluene in yellow crystals, melting at 129°. It is absolutely devoid of basic properties, being insoluble in hydrochloric acid, even when concentrated, and reacts neither with methyl iodide nor with methyl sulphate.

Supposing that, in spite of its properties, it might constitute the required nitroveratryldihydro*iso*quinoline, we submitted it to reduction in the hope of converting it into aminoveratryltetrahydro*iso*quinoline. It was therefore heated with stannous chloride and concentrated hydrochloric acid. On cooling, a well-defined, crystalline tin salt, sparingly soluble in cold water, was obtained, which, when decomposed with hydrogen sulphide, yielded a colourless, crystalline hydrochloride, freely soluble in water. This hydrochloride gives a precipitate with auric chloride and platinic chloride, but not with picric acid. The addition of an alkali causes the separation of an oily base ammoniacal in odour.

This base is a primary one (carbylamine reaction), and in order to identify it, we transformed it, according to the Schotten-Baumann reaction, into its benzoyl derivative. The latter crystallises from alcohol or water in spangles, melting at 118°. Its analysis (Found, $C=80.06$; $H=6.60$) leads to the formula of benzoyl-β-phenylethylamine ($C_{15}H_{15}ON$ requires $C=79.96$; $H=6.22$ per cent.), and evidently the two substances are identical, for a mixture of the two melts at 118°, the melting point of each of them separately. The base obtained by the reduction of the yellow compound, melting at 129°, is therefore β-phenylethylamine. It consequently follows that the so-called yellow substance is in no way a derivative of *iso*quinoline, and that the treatment of 2-nitrohomoveratroyl-β-phenylethylamine with phosphoric oxide does certainly bring about the elimination of water, but without cyclisation. The dehydro-product is still a derivative of β-phenylethylamine, capable of regenerating that base by reduction, accompanied by hydrolysis. We have already indicated our views on its constitution.

We may add that we have attempted, with the same negative result, the cyclisation of the simpler compound:



$CH_2Ph{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2 \quad NO_2$.

This substance, obtained by the action of the chloride of *o*-nitrophenylacetic acid on β-phenylethylamine, forms colourless crystals, melting at 97—99°:

0·1207 gave 0·2986 $CO_2$ and 0·0608 $H_2O$. $C=67.47$; $H=5.64$.

$C_{16}H_{16}O_3N_2$ requires $C=67.58$; $H=5.67$ per cent.

When heated for half an hour with excess of phosphoric oxide in xylene solution, it undergoes no change whatever.

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# XCIX.—*A Criticism of Some Recent Viscosity Investigations.*

### By Eugene Cook Bingham.

As scientific knowledge increases in volume, it becomes increasingly difficult to become fully informed even in the narrow field within which one happens to be working. It therefore happens that truth once discovered is apparently lost, only to be rediscovered and lost again, instead of becoming at once the property of all, with the consequent saving of time and energy. Nowhere is this more noticeably true, perhaps, than in the study of viscosity. The reason may be that few workers have been interested in the property of viscosity for its own sake, but hundreds of researches have been carried out in the hope of throwing light upon problems suggested by other properties, such as conductivity, dissociation, etc.

Viscosity data are in a rather unsatisfactory condition. Only part of the data is given in absolute units, so that comparisons are difficult. Furthermore, much of the data, which is given in absolute units, was obtained from measurements which were not themselves absolute, but relative, and it appears that in relative measurements the necessary corrections have often been omitted whereby reduction to absolute units could be effected with sufficient precision. Thus, test observations by workers using the same liquid for successive observations have been known (Přibram and Handl, *Sitzungsber. K. Akad. wiss. Wien*, 1878, **78**, ii, 113; compare Thorpe and Rodger, *Phil. Trans.*, 1894, **185**, *A*, 403) to differ by over 10 per cent. The earlier absolute measurements were also somewhat discordant, owing to the fact that several important corrections were overlooked. As a result of these conditions, several (Knibbs, *J. Roy. Soc. New South Wales*, 1896, **30**, 186; compare *Zeitsch. physikal. Chem.*, 1912, **80**, 685; Traube, *Ber.*, 1886, **19**, 871) have expressed the doubt as to the possibility of the accurate measurement of viscosity. However, it has now been proved that with the necessary corrections which can be easily applied, perfectly definite and very accurate values may be obtained. Perhaps the best proof of this is the fact (compare *Zeitsch. physikal. Chem.*, 1912, **80**, 685) that the mean deviation from the mean values for water from 0° to 100° of six different investigators is only 0·3 per cent.

In view of the scantiness of existing material, it is therefore a matter for particular regret when a research, planned with the view toward the highest possible accuracy, is carried out without the knowledge of conditions and corrections necessary for making the results truly absolute, and therefore comparable with the data of other observers, and of the appropriate methods for interpreting the results.

The recent work of Applebey (T., 1910, **97**, 2000) may be chosen as an illustration because this work has been carried out with admirable care and ingenuity. The attempt was made to reduce the error to less than 0·1 of 1 per cent., and control experiments are given to prove that this high degree of precision was actually attained. Applebey states on p. 2013: "It is to be noted that no kinetic energy correction is to be applied in calculating the results of experiments with viscometers in which the capillary opens out into a reservoir of the same liquid. The correction calculated by earlier observers (Hagenbach, *Pogg. Ann.*, 1860, **109**, 385; Finkener, see Gartenmeister, *Zeitsch. physikal. Chem.*, 1891, **6**, 524) is only applicable when the liquid flows from the capillary directly into the air. In viscometers of the Ostwald type, however, the gain of kinetic energy at the beginning of the capillary is balanced by the loss of kinetic energy an emerging from the capillary into the lower bulb. The net increase in kinetic energy is therefore negligible. . . ." The present author holds that the correction which is necessary when the capillary opens into the air is not a kinetic energy correction at all, but rather a correction for the loss of pressure due to the capillary attraction at the opening of the tube. This correction is dependent upon the shape of the end of the tube, and it fluctuates with the size of the drop at a given moment, hence it is very difficult to estimate. Naturally this correction is avoided in viscometers of the Ostwald type. It would be presumptuous to attempt to prove that the kinetic energy correction does indeed apply to the Ostwald type of viscometer in view of the published work of Neumann ("Vorträge über Hydrodynamik"), Jacobson (*Arch. f. Anat. u. Physiol.*, 1860, **80**), Couette (*Ann. chim. Phys.*, 1890, [vi], **21**, 433), Wilberforce (*Phil. Mag.*, 1891, [v], **31**, 407), Knibbs (*J. Roy. Soc. New South Wales*, 1895, **29**, 77; 1896, **30**, 186), Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, *A*, 397), Boussinesq (*Compt. rend.*, 1890, **110**, 1160, 1238; 1891, **113**, 9, 49), and Brillouin ("La Viscosité," Gauthier-Villars, 1907, p. 131), in addition to those mentioned by Applebey. A simple statement may, however, serve to make the necessity for the correction apparent. For sake of simplicity, let us assume that the liquid flows through a horizontal capillary of uniform bore connecting two reservoirs. If $P'$ is the hydrostatic pressure at the entrance of the capillary and $P''$ at the exit, then $P'-P''$ is the measure of the pressure used up in overcoming the viscous resistance. Near the entrance to the capillary, however, the liquid is in accelerated motion for a short distance. In gaining this kinetic energy, the pressure falls from $P$ to $P'$, hence the whole loss in pressure, measured by the difference in heads in the two reservoirs, is equal to $P-P'+P'-P''=P-P''$. The mean velocity at the exit end of the tube is the same as at every other cross-section of the tube, and its inertia carries it a considerable distance into the body of the liquid in the lower reservoir. By means of eddies, this motion finally becomes disordered, that is, it disappears as heat, and not as potential energy, as Applebey supposes. Finally, Bingham and White (*Zeitsch. physikal. Chem.*, 1912, **80**, 684) measured the viscosity of water under the above conditions with a capillary which was afterwards cut into several pieces so as to give conditions for interrupted flow, and it was found that the kinetic energy corrections as demanded by the theory are directly proportional to the number of capillaries in series.

By varying the pressures, Applebey finds that the product of the pressure multiplied by the time of transpiration is approximately constant only when the time is not less than 400 seconds. He apparently assumes (p. 2005) that the inconstancy of the product $p \times t$ for smaller values of $t$ is "due to the fact that above a certain limiting velocity the flow of liquid in the viscometer is not steady, but that some of the potential energy is expended in forming eddies within the liquid." There can be no doubt that the product $p \times t$ will become inconstant when the velocity of efflux becomes sufficiently great, but the cause in Applebey's experiments may be due to the kinetic energy correction, which he has considered negligible. His capillary had a radius of 0·2 mm., and the transpiration volume was 7 c.c. Therefore the velocity of efflux could never have been greater than:

$$\frac{V}{\pi r^2 t} = \frac{7}{3{\cdot}1416 \times (0{\cdot}02)^2 \times 400} = 14 \text{ cm. per second.}$$

Now, Osborne Reynolds (*Phil. Trans.*, 1883, **174**, 935; 1886, **177**, *A*, 157) has given an expression for the critical velocity above which eddy currents may be formed. It is $\frac{700}{r\rho\phi}$. For water at 25° the fluidity ($\phi$) is equal to 112·0 and the density ($\rho$) is not far from unity, hence the critical velocity is 312 cm. per sec. All of Applebey's solutions were more viscous than water at 25°, hence his velocities were not one-twentieth of the critical value where the motion becomes sinuous.

Moreover, not only was the fancied danger of sinuous motion unreal, but the very slow velocities which were used tended to aggravate a source of error which in this particular case became very annoying (pp. 2010, 2011, and 2012). He says in particular that "in spite of all precautions, the tubes frequently became contaminated with dust." At very low velocities, particles of dust could more easily find lodgment in the capillary, and thus vitiate the determination. That higher velocities would have served to keep the capillary clean is indicated by the results of several experimenters,* where with reasonable care to avoid the presence of dust the successive observations are almost invariably quite satisfactory.

The equation for viscosity containing the correction for the loss in kinetic energy is:

$$\eta = \frac{\pi g r^4 t p}{8 V l} - \frac{m \rho V}{8 \pi t l},$$

where $\pi = 3{\cdot}1416$, $g$ is the acceleration due to gravitation, $r$ the radius of the capillary, $l$ its length, $t$ the time of transpiration, $V$ the volume passing through the capillary, $p$ the corrected pressure in grams per sq. cm., $\rho$ is the density of the liquid, and $m$ is a constant which has been approximated to be 1·12 (compare *Zeitsch. physikal. Chem.*, 1912, **80**, 670). The correction for kinetic energy is expressed by the second term of the right-hand member of the equation. For a given instrument, the equation takes the form:

$$\eta = ctp - c'\rho/t,$$

where $c$ and $c'$ are constants. Since the density cannot be changed *ad libitum*, the only way to make the kinetic energy correction negligible is to make the time of transpiration very large. This is exactly what was done by Applebey, and I believe that his measurements possess a higher degree of trustworthiness than many of the measurements which have been made with this type of apparatus. Apart, however, from the danger of partial clogging of the capillary, such lengthening of the time of transpiration is objectionable, both on account of the increased difficulty in proper temperature regulation and in the loss of time occasioned. Some of Applebey's measurements required over two hours for a single transpiration, whilst the minimum was seven minutes. With several modern forms of apparatus, less than half of the minimum time used by Applebey is required, and by employing variable pressure the time consumed with the more viscous liquids need not necessarily be any greater. With the Ostwald type of apparatus, having a pressure which is not variable at will, the loss of time with the more viscous liquids makes the use of a series of viscometers, with the consequent loss of time in calibration and additional sources of error, almost a necessity.

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* Particularly worth study in this connexion are the very consistent results of Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, *A*, 397

If two liquids having viscosities $\eta_1$ and $\eta_2$ transpire through a given instrument in times $t_1$ and $t_2$ respectively, we have the relation:

$$\frac{\eta_1}{\eta_2}=\frac{ct_1p_1-c'\rho_1/t_1}{ct_2p_2-c'p_2/t_2},$$

and if $t_1$ and $t_2$ are both very large, and also if, in addition, $\eta_1$ is nearly equal to $\eta_2$, this expression can be reduced to the form:

$$\eta_1=\eta_2\frac{t_1p_1}{t_2p_2},$$

which is the formula given by Ostwald and Luther ("Physiko-chemische Messungen," 2nd ed., Engelmann, p. 259 *et seq.*), and generally used for calculating viscosities with the Ostwald viscometer. Of course, these two expressions are not generally identical, and it is the oversight of this fact which seems to have often led observers into error. It is obvious that in using the Ostwald instrument a ready means of control can be obtained by measuring the viscosities of several different liquids, or of the same liquid at considerably different temperatures to see how closely the results would agree with those by the absolute method. The results of such tests have only rarely been given, and then they do not inspire confidence (*Amer. Chem. J.*, 1911, **46**, 281; compare Findlay, *Zeitsch. physikal. Chem.*, 1909, **69**, 203).

In the Ostwald type of apparatus it seems to be regarded as of great importance that the height of the hydrostatic column should be small, thus keeping the velocity of flow small while using a capillary of fairly large diameter. In Applebey's apparatus this height was 10·8 cm., so that an error of 0·01 cm. in adjusting the height would cause an appreciable error. It is probably to avoid this source of error that the bulbs above and below the capillary are made large. There is, however, comparatively bad drainage on the surfaces which depart widely from the vertical, the adjustment of temperature is slow in large, spherical masses, and the time of transpiration is made unnecessarily large. Finally, with this method the specific gravity of each liquid at every temperature which it is proposed to study must also be known to 0·1 of 1 per cent.*

In the interpretation of viscosity data, it may be pointed out that many years ago it was shown (T., 1897, **71**, 374) that viscosity curves of mixtures are rarely linear, but that the values are usually less than they should be on the usual assumption that viscosities are normally additive. It was, however, pointed out (Jones and Bingham, *Amer, Chem. J.*, 1905, **34**, 545; Bingham, *ibid.*, 1906,

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* In some other forms of apparatus it is only necessary to know the specific gravity approximately, since it is only used in calculating correction terms.

**35**, 195; *J. Amer. Chem. Soc.*, 1911, **33**, 1257; *Physical Review*, 1912, **35**, 407) that theoretically *we should expect fluidities to be additive, so that viscosities cannot be additive as has been assumed*, but must normally be hyperbolic. Existing viscosity data fully confirm this view. Numerous papers have been published (for a partial bibliography compare *Physical Review*, 1912, **35**, 407; also White, *J. Ind. Eng. Chem.*, 1912, **4**, 267) showing that fluidities are satisfactorily additive, provided that association and dissociation do not enter as disturbing factors. It is perhaps unfortunate that this proviso must be attached, since it seems to offer an opportunity for "making the facts fit the theory." The assumption of association should, however, never be resorted to without supporting evidence. Thus it would be difficult to explain how the fluidity of a mixture could be greater than the value obtained from the linear fluidity curve unless one or more of the components of the mixture are themselves associated. If, however, on mixing two components heat is evolved, contraction occurs, and the fluidity is less than that calculated from the linear fluidity curve, a suspicion may justly be aroused that the abnormality is due to combination. When it can be shown that the maximum heat evolution, contraction, lowering of the vapour pressure, and lowering of the fluidity all coincide in the same mixture, and that, moreover, this mixture contains simple molecular proportions of the constituents, and particularly when it can be shown that the combination between the components obeys the law of mass action, as in the case of chloroform and ether (*Zeitsch. physikal. Chem.*, 1913, *in press*; compare *Physical Review*, 1913, **36**, 112 *et seq.*), then there is not only justification for the assumption of combination, but the cases excepted in the above proviso become positive aids in substantiating the hypothesis that fluidities and not viscosities are additive.

The authors of several recent papers have accepted the earlier assumption that viscosities are additive, without a reference to the work just cited. Thus, Baker (T., 1912, **101**, 1409), in a valuable paper on the viscosities of mixtures of alcohols and ethers. notes with surprise that the values of the viscosity are less than would be expected on the old hypothesis. In view of the later hypothesis, this fact is not only not surprising, but has been predicted beforehand for most mixtures. He says, "In nearly all cases there is a considerable departure from the calculated values, and in two cases a minimum value for the viscosity was observed. These results indicate that when the associated alcohols are mixed with ethers, dissociation of the former takes place, and therefore the viscosity of the mixture is less than that calculated from the viscosity of the components." I do not question the correctness of Baker's conclusion that dissociation does occur in at least some of the cases discussed by him; but the reading of his discussion is not so convincing as it might be, since he does not attempt to establish his fundamental assumption that viscosities are normally additive in homogeneous mixtures.

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# C.—*Reactions of Halogen-substituted Acids. Effect of Alkalis in Methyl-alcoholic Solution on Bromoacetic, α-Bromopropionic, and Monobromosuccinic Acids.*[*]

## By ERIK HÖST MADSEN.

IN reactions between organic halogen compounds and alcoholic alkalis, it is customary to use sodium ethoxide in order to bring about substitution, and alcoholic potassium hydroxide for the elimination of hydrogen haloid. Hitherto, however, no theoretical or practical reasons have been given for using the different reagents in the respective cases.

Nef (*Annalen*, 1899, **309**, 126) was the first to investigate the reactions of a large number of alkyl haloids, and in all cases he obtained the same results, whether sodium alkyloxides or alcoholic solutions of potassium hydroxide were used. In many cases elimination of hydrogen haloid and substitution took place simultaneously, and he concluded that the action of the two reagents was essentially the same, the course of the reaction depending only on the position of the halogen atom and on the character of the alkyl group.

The halogen-substituted acids behave similarly. In those of them which contain two or more halogen atoms, it is possible for the same reagent to bring about both kinds of reaction simultaneously at the different halogen atoms. Thus, on treating dibromopropionic acid with two molecules of sodium ethoxide, or of potassium hydroxide in alcoholic solution, hydrogen bromide is eliminated, with the formation of monobromoacrylic acid (Merz, "Studien über gebromte Propionsäuren," Erlangen, 1889, p. 15). When three molecules of potassium hydroxide are used in alcoholic solution, replacement of the second bromine atom also occurs, with the formation of ethoxyacrylic acid.

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[*] For fuller details, reference should be made to the author's book, "Kritiske Studier over Alkoholaters og Basers Indvikning paa organiske Halogenforbindelser." Copenhagen, 1912, Pp. 92—157.

The results of some investigations seem to indicate, however, that sodium ethoxide and alcoholic potassium hydroxide may act differently. Thus, Hell and Lauber (*Ber.*, 1874, **7**, 560) found that ethyl $\alpha$-bromobutyrate and hot alcoholic potassium hydroxide gave mainly crotonic acid, with very little ethoxybutyric acid. Duvillier (*Ann. Chim. Phys.*, 1879, [v], **17**, 532) found that the same ester gave only ethyl ethoxybutyrate when sodium ethoxide was used.

It is probable that the above differences are due to variations in temperature and concentration of the reagents in the different experiments, and not to any essential difference in the actions of sodium ethoxide and alcoholic potassium hydroxide. For example, Schreiner (*Annalen*, 1879, **197**, 1), in the reaction between ethyl bromobutyrate and sodium ethoxide, in one experiment obtained ethyl crotonate, and in another, ethyl ethoxybutyrate.

The above few examples would indicate that no distinction can be drawn between alcoholic solutions of hydroxides and alkyloxides of the alkali metals, with respect to the elimination of hydrogen haloid or to the process of substitution. Both reactions are due to the alkyloxide, which is the only compound, except alcohol, that is common to both solutions when absolute alcohol is used.

In alcoholic potassium or sodium hydroxide solution, an equilibrium exists in accordance with the equation:

$$KOH + C_2H_5{\cdot}OH \rightleftarrows C_2H_5{\cdot}OK + H_2O.$$

The position of equilibrium is not known, but the results of investigations hitherto carried out would indicate that in such solutions most of the alkali metal is present as the alkyloxide, and that a large quantity of water is necessary to decompose this compound. The presence of water in such solutions has the effect that they are able to react in such a way that the halogen is substituted by the hydroxyl group, as well as by the ethoxy-group. The alkyl haloids are not suitable for observing the simultaneous occurrence of these two reactions, since even with 50 per cent. aqueous alcoholic solutions the formation of ether is the main reaction.

The halogen-substituted acids, in most cases, give either alkyloxy- or else unsaturated acids, or generally a mixture of both, when treated with alcoholic potassium hydroxide. In some cases, however, the hydroxide character of the solution is very marked, hydroxy-acid being formed in addition to the alkyloxy-acid; as examples may be quoted bromo*iso*succinic acid (Tanatar, *Annalen*, 1893, **273**, 40) and bromo*iso*butyric acid (Bischoff, *Ber.*, 1891, **24**, 1041).

Walden, in his well-known investigations on optical inversion (*Ber.*, 1896, **29**, 133; 1897, **30**, 2795, 3146; 1899, **32**, 1833), obtained only malic acid from the optically active halogen-substituted succinic acids, no matter whether the alkali used was in aqueous or in methyl-alcoholic solution. Walden was not concerned as to the reason why the formation of the methoxy-acid was totally restrained, confining himself to the optical results; the author has consequently submitted the matter to further investigation in order to find out how much water (in the form of water or hydroxide) the alkaline solution must contain in order to do away completely with the formation of methoxy-acid. Inactive bromosuccinic acid was used, since optical properties were of no importance in this connexion.

Preliminary experiments having shown that the reaction took place much more rapidly in methyl-alcoholic sodium hydroxide solution than in a solution of sodium ethoxide in absolute methyl alcohol, it seemed probable that there would be some connexion between the reaction-velocity and the products formed when the alcoholic solution used contained varying quantities of water. In order to test this supposition more thoroughly, the investigation was extended to include α-bromopropionic and bromoacetic acids, as well as monobromosuccinic acid.

It is necessary to know exactly the composition of the solution used. In the case of sodium methoxide solution, there is no difficulty in this connexion if absolute methyl alcohol is used, but if the methyl-alcoholic solution of sodium hydroxide is prepared by dissolving the hydroxide in the alcohol, the water content of the solution is not known. The method adopted in the latter case was to add a definite quantity of water to the methoxide solution, or else to dissolve sodium in a mixture of known composition of methyl alcohol and water.

## EXPERIMENTAL.

### *Purification of Substances Used.*

Anhydrous methyl alcohol was obtained by thrice repeated distillation from metallic calcium (compare Klason and Norlin, *Arkiv Kem. Min. Geol.*, 1905, **2**, 24).

Bromoacetic acid was purified by recrystallising Kahlbaum's product from one-fifth of its weight of benzene, it being afterwards dried over phosphoric oxide and paraffin. The equivalent was 139·6 (theory 139·0).

α-Bromopropionic acid was purified by drying Kahlbaum's product in a current of air at 125°, distilling it under diminished pressure, and causing it to crystallise by cooling with solid carbon dioxide and ether. The crystals were centrifugalised for fifteen minutes at the ordinary temperature, kept overnight in a vacuum desiccator, and again centrifugalised the next day, after which they were dried for nearly a week in a vacuum desiccator. The melting point was 25·7—27·1°, the equivalent being 153·6° (theory 153·0°).

Commercial monobromosuccinic acid contains fumaric acid. It was purified in two ways: (1) According to Müller's method (*Zeitsch. physikal. Chem.*, 1902, **41**, 486), by solution in water and extraction of the fumaric acid with ether, the process being repeated four times. (2) By fractional recrystallisation of the acid, which had been treated twice according to Müller's method. Thirty-nine grams of the acid were dissolved (incompletely) in 100 c.c. of acetone, and to the filtrate 90 c.c. of benzene were added. The solution was then concentrated until it crystallised on cooling; the first fraction which separated contained all the fumaric acid, the succeeding fractions consisting of practically pure monobromosuccinic acid. The product (1), afterwards referred to as the extracted acid, had an equivalent of 98·3, the product (2), called the recrystallised acid, an equivalent of 98·6—98·8 (theory 98·5).

### *Examination of Reaction Products.*

The reaction product to be expected may consist of methoxy- or hydroxy-acids, or a mixture of both. Since it is impossible to isolate the respective acids without considerable loss of substances, the method adopted was to estimate the percentage of the methoxy-group in the product obtained. The actual formation of hydroxy-acid in any particular case could only be proved by isolating it, owing to the absence of distinctive tests for identification.

In all cases the solutions used were prepared with absolute methyl alcohol, and were 0·1 molecular with respect to the sodium salt of the acid; they also contained sodium methoxide and water in such proportions that the reaction mixture was represented by 1 mol. of the sodium salt of the acid, 1 mol. of sodium methoxide, and 0, 1, or 3 mols. of water. The respective solutions will be called *A*, *B*, or *C*, according as the proportion of water is 0, 1, or 3 mols. The reaction took place in sealed tubes, which were heated in a thermostat at 64°; when the reaction was finished, the contents of each tube were poured into a dish and evaporated to dryness on the water-bath. The last traces of methyl alcohol were removed by dissolving the residue in 10 c.c. of water, neutralising with hydrochloric acid, and again evaporating to dryness. The residue was powdered, well mixed, and the percentage of methoxyl determined in a weighed portion. The accuracy of the method was checked by a blank experiment with succinic acid.

The results obtained with bromosuccinic acid are shown in the following table:

| | *A.* | *B.* | *C.* |
|---|---|---|---|
| Mols. of substance used | 0·01 | 0·01 | 0·01 |
| Time | 21 days | 95 hours | 67 hours |
| Weight of residue (grams) | 2·86 | 2·71[*] | 3·02 |
| Grams of methoxyl in residue | 0·00408 | 0·00068 | 0·00029 |
| Per cent. of methoxy-acid formed | 40·8[†] | 6·8 | 2·9 |

Experiment *C* confirmed the results obtained by Walden, but for complete verification it was necessary to isolate the malic acid. This was done as follows: 3·94 grams (0·02 mol.) of recrystallised bromosuccinic acid were dissolved in 100 c.c. of absolute methyl alcohol; after the addition of a solution of 1·38 grams (0·06 mol.) of sodium in a mixture of 1·08 grams (0·06 mol.) of water and 100 c.c. of methyl alcohol, the mixture was heated for seven hours on the water-bath under reflux, a calcium chloride tube being attached to the condenser. On the next day the precipitated sodium salts were collected (by centrifugalising), washed with absolute methyl alcohol, and dried in a vacuum, after which the salts were dissolved in 2 grams of water, and the fumaric acid precipitated with a little dilute sulphuric acid. After collecting the fumaric acid, the filtrate was diluted to 40 c.c., and the last traces of fumaric acid extracted with ether (total weight of fumaric acid = 0·34 gram). The solution was then freed from sulphuric acid by the addition of the exact equivalent of barium hydroxide, the malic acid precipitated as the lead salt, the precipitate washed with 60 per cent. alcohol, and then treated with hydrogen sulphide. The weight of racemic malic acid left on evaporation of the filtrate from the lead sulphide, any inorganic salts present having been removed by redissolving the acid in ether, was 0·59 gram. (Found, C = 36·15; H = 4·76. Calc., C = 35·81; H = 4·52 per cent.) The filtrate from the sodium salts still contained some fumaric (0·03 gram) and malic acids. By evaporation, extraction of the residue with acetone, renewed evaporation and fractional extraction of the residue with ether, 0·29 gram of yellow, but nearly pure, malic acid was obtained. Thus the total amount of fumaric acid formed was 0·37 gram (16 per cent. of the theory) and 0·88 gram of malic acid (33 per cent. of the theory).

These experiments confirm Walden's results, and disclose the noteworthy fact that one equivalent of water in the presence of a very large excess of methyl alcohol enters almost quantitatively into reaction.

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[*] A little of the residue was lost, so that this number is too low.

[†] In the case of *A*, 64 per cent. of the bromosuccinic acid had reacted in 9 days, and 71 per cent. in 21 days, some fumaric acid being formed as well as methoxysuccinic acid. Before the evaporation, 5 c.c. of water were added to prevent further formation of methoxy-acid, and if the percentage of methoxy-acid formed is corrected to 100 per cent. reaction of the bromosuccinic acid, the number 57·5 is obtained instead of 40·8.

The results obtained with α-bromopropionic and bromoacetic acids are given in the following table:

| | α-Bromopropionic acid. | | Bromoacetic acid. | |
|---|---|---|---|---|
| | *A.* | *C.* | *A.* | *C.* |
| Mols. of substance used ............ | 0·005 | 0·005 | 0·005 | 0·005 |
| Time (hours)............................ | 97 | 97 | 25 | 25 |
| Weight of residue (grams) ......... | 1·13 | 1·12 | 1·13 | 1·14 |
| Grams of methoxyl in residue ... | 0·00465 | 0·00438 | 0·00461 | 0·00484 |
| Per cent. of methoxy-acid formed | 93·0 | 87·6 | 92·1 | 96·8 |

Thus in all cases about 90 per cent. of the theoretical quantity of methoxy-acid was formed, the presence of water having practically no effect on the course of the reaction.

### *Measurements of Velocity of Reaction.*

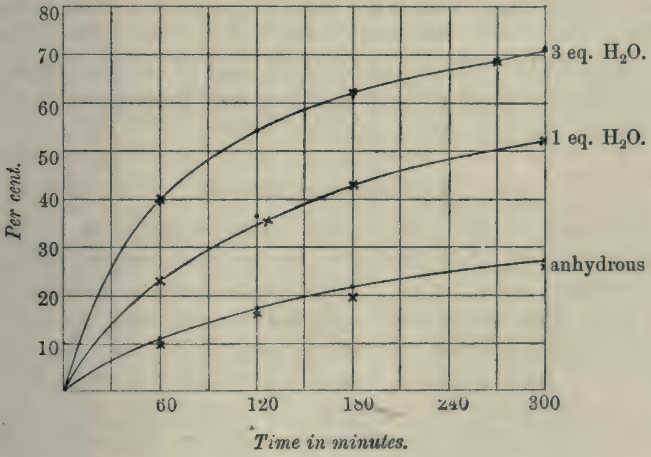
The reaction mixtures used corresponded with those given in the first part of this paper. They were made as follows, the acid and alkaline solutions being prepared separately. The acid solutions were 0·2-molar in all cases, the sodium methoxide solutions being as follows: (*a*) 0·4*N* for the experiments with monobasic acids, I anhydrous, II with 0·2 mol. water per litre, III with 0·6 mol. water per litre; (*b*) 0·6*N* for the experiments with the dibasic acid, I, II, and III being as in (*a*). When equal volumes of the acid and alkaline solutions were mixed, solutions were thus obtained corresponding with *A*, *B*, and *C* (p. 968). A fourth solution, *D*, was also used, which corresponded with *A*, but contained, in addition, 0·5 mol. of sodium bromide per litre. The solutions were mixed at the ordinary temperature, and then placed in sealed tubes in a thermostat at 64°, each tube containing about 20 c.c. of solution. The times, *t*, were calculated from a point ten minutes after the tubes were placed in the thermostat, and the concentration, *a*, of the reacting substances from the original titre of the acid solution; $k_1$ and $k_2$ are the constants calculated according to reactions of the first and second orders respectively. In calculating $k_2$, the factor 0·93948 was used to correct for alteration in volume on heating, no correction being applied in calculating $k_1$.

The following are the results for monobromosuccinic acid, the figures given relating to those obtained with the extracted acid (see p. 968).

| | *A*:— | | | | | *B*:— | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *t* ........... | 0 | 60 | 120 | 180 | 300 | 0 | 60 | 127 | 180 | 300 |
| $200\,(a-x)$ | 18·13 | 16·43 | 15·21 | 14·55 | 13·45 | 17·62 | 13·55 | 11·42 | 10·09 | 8·41 |
| $k_2 \times 10^3$ ... | — | 20·2 | 18·8 | 16·0 | 13·6 | — | 60·5 | 51·6 | 50·1 | 44·1 |

| | *C*:— | | | | *D*:— | | | |
|---|---|---|---|---|---|---|---|---|
| *t* ............... | 0 | 60 | 180 | 270 | 0 | 60 | 200 | 270 |
| $200\,(a-x)$ ... | 16·92 | 10·18 | 6·43 | 5·26 | 16·11 | 13·24 | 10·83 | 9·91 |
| $k_2 \times 10^3$ ...... | — | 139 | 114 | 103 | — | 47·7 | 32·2 | 30·6 |

The results show that the reaction is accelerated by the addition of water (see diagram). The relation between the reaction velocities for *A*, *B*, and *C* is approximately 1 : 4 : 8, but cannot be given exactly, since the values of $k_2$ decrease continuously. That the decrease is not due to impurities in the acid is shown by the fact that both the extracted (× in diagram) and recrystallised acids (· in diagram) give the same results. Nor is the decrease due to sodium bromide formed during the reaction, as shown by experiment *D*, although the addition of sodium bromide has a noticeable effect on the velocity.



The results obtained with α-bromopropionic acid are as follows:

| | *A*:— | | | *B*:— | | | | |
|---|---|---|---|---|---|---|---|---|
| *t* ............ | 0 | 60 | 150 | 0 | 60 | 120 | 181 | 240 |
| $200\,(a-x)$ | 19·60 | 15·77 | 11·62 | 19·51 | 15·57 | 12·86 | 10·45 | 8·86 |
| $k_1 \times 10^5$ ... | — | 362 | 348 | — | 376 | 347 | 345 | 329 |

| | *C*:— | | | | | *D*:— | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *t* ............ | 0 | 63 | 120 | 180 | 241·5 | 0 | 60 | 120 | 180 | 240 |
| $200\,(a-x)$ | 19·50 | 15·44 | 12·63 | 10·28 | 8·48 | 19·36 | 16·12 | 13·65 | 11·55 | 10·11 |
| $k_1 \times 10^5$ ... | — | 370 | 362 | 356 | 345 | — | 305 | 291 | 287 | 271 |

The figures show that the presence of water has no effect on the velocity of reaction, the mean values of $k_1 \times 10^5$ being 355, 349, and 358 in *A*, *B*, and *C* respectively. The constants decrease slightly during the course of the reaction. When the strength of the (anhydrous) reaction mixture used is one-half that of *A*, they have a mean value of 280, which is somewhat lower than that for the more concentrated solution. However, if the times necessary for the reaction to proceed to an extent of 50 per cent. are calculated in the two cases (*A* and 0·5*A*), they are found to be 233 and 199 minutes, giving a ratio of 1·17, which is sufficiently close to 1 to warrant the reaction being considered as one of the first order.

With bromoacetic acid, the results are as follows:

*A*:—

| $t$ ………… | 0 | 60 | 110 | 161 | 230 |
|---|---|---|---|---|---|
| 200 $(a-x)$ | 18·03 | 10·51 | 7·82 | 6·37 | 4·86 |
| $k_2 \times 10^3$ … | — | 141 | 140 | 134 | 139 |

*B*:—

| $t$ ………… | 0 | 60 | 105 | 150 | 240 |
|---|---|---|---|---|---|
| 200 $(a-x)$ | 17·91 | 10·63 | 8·07 | 6·46 | 4·78 |
| $k_2 \times 10^3$ … | — | 136 | 138 | 140 | 136 |

*C*:—

| $t$ ………… | 0 | 60 | 106 | 150 | 241 |
|---|---|---|---|---|---|
| 200 $(a-x)$ | 17·96 | 1048 | 8·08 | 6·55 | 4·76 |
| $k_2 \times 10^3$ … | — | 141 | 137 | 138 | 136 |

*D*:—

| $t$ ………… | 0 | 30 | 45 | 75 | 127 |
|---|---|---|---|---|---|
| 200 $(a-x)$ | 15·35 | 8·75 | 7·13 | 5·38 | 3·64 |
| $k_2 \times 10^3$ … | — | 349 | 355 | 343 | 351 |

The mean values of $k_2 \times 10^3$ for *A*, *B*, and *C* are respectively 139, 138, and 138, so that in this case also the presence of water has no effect on the velocity of reaction.

### *Discussion of Results.*

In the case of the three acids examined there is evidently a connexion between the effect of water on the products formed and on the velocity of reaction. Whether the sodium salts of bromoacetic and α-bromopropionic acids are treated with an anhydrous methyl-alcoholic solution of sodium methoxide, or with one containing 1—3 equivalents of water, a practically quantitative yield of the methoxy-acid is obtained; in accordance with this, the presence of water has no effect on the velocity of reaction. In the case of monobromosuccinic acid, however, the presence of water alters both the velocity of reaction and the products of reaction.*

It is noteworthy that when the reaction is of the first order, the presence of sodium bromide, one of the products of reaction, decreases slightly the velocity of reaction, whereas when of the second or higher order, a considerable increase in velocity takes place.

The effect of water on the velocity of these reactions may be compared with its effect on the reaction between alkyl haloids and sodium alkyloxides (Lobry de Bruyn and Steger, *Rec. trav. chim.*, 1899, **18**, 311; *Zeitsch. physikal. Chem.*, 1904, **49**, 336), where the velocity is decreased by the addition of water; with small quantities of water the change is only relatively small, the velocity-constant in the case of ethyl iodide decreasing from 0·189 to 0·155 on the addition of 10 per cent. of water. In the case of the saponification of esters (Kremann, *Monatsh.*, 1905, **26**, 279), the addition of water has a much greater influence. In 0·05-molar solution the presence of 0·9 gram of water per litre increased the reaction velocity to four times its original value.

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* It is well to point out that these experiments show that conclusions based on a comparison of reaction velocities in mixed solvents must be drawn very cautiously.

Whilst the results of the present investigation throw light on the problem it was the object of the author to examine, it is evident that the mechanism of the reactions taking place is in need of explanation. The constitution of the three acids would lead one to suppose that they would behave similarly; nevertheless the order of reaction is different in every case. That the reaction with bromoacetic acid is of the second order is in accordance with the chemical equation. The reaction with α-bromopropionic acid is of the first order, however, and one may assume that the reaction does not take place between the salt (sodium α-bromopropionate) and sodium methoxide, but between the salt and alcohol, the concentration of the latter remaining constant. The reaction between sodium bromosuccinate and sodium ethoxide is apparently of a higher order than the second. It is possible, according to the usual interpretation, that in this case two reactions are proceeding simultaneously with different and measurable velocities, namely: (1) the formation of an intermediate compound, and (2) its decomposition (compare Senter, *Ber.*, 1912, **45**, 2318; Senter and Ward, T., 1912, **101**, 2534; Holmberg, *Ber.*, 1912, **45**, 1713). It is possible, and even probable, that the decomposition of the intermediate compound by alcohol takes place with much more difficulty than the decomposition by water, so that mainly hydroxy-acid is formed, even in the presence of only small quantities of water, which is in accordance with the experimental results. In this connexion attention should be called to the fact that monobromosuccinic acid gives less than the calculated yield of methoxysuccinic acid when treated with anhydrous sodium methoxide solution. This fact is not easy to explain unless the formation of an intermediate product is assumed which is relatively stable in the presence of methyl alcohol, and therefore able to exist to some extent in a reaction mixture which contains only that alcohol as solvent, but is decomposed at once when water is added.

The author desires to express his thanks to Prof. E. Biilmann, in whose laboratories the experimental part of this investigation was carried out.

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# CI.—*Cyanogen Bromide and Cyanogen.*

By Augustus Edward Dixon and John Taylor.

Cyanogen bromide, in cold aqueous solution, or in the presence of such dilute acids as do not of themselves chemically decompose it, shows no evidence of suffering ionic dissociation. The dilute aqueous solution has the same odour as the solid compound; even after long keeping it yields with silver nitrate no turbidity; it is neutral to litmus, and the pungent vapour fails to give the guaiacum and copper sulphate reaction for hydrogen cyanide; moreover, the solution is a very feeble conductor of electricity.

Although the mixture produced by treating cyanogen bromide with alkali hydroxide contains but alkali bromide and alkali cyanate, Chattaway and Wadmore are of opinion (T., 1902, **81**, 199) that hypobromite must first be formed, and then reduced.

That cyanate is not directly formed in the reaction with alkali hydroxide is proved from the following facts:

(1) Alkali cyanate is not reduced to cyanide by hydriodic acid, ferrous sulphate and alkali, sulphurous acid, alkali sulphite, or even by treatment with aluminium and alkali hydroxide. Further, it has no action on carbamide, either alone or in presence of alkali.

(2) If cyanogen bromide is treated with alkali iodide, followed by alkali, the mixture contains cyanide, but no cyanate, and, when acidified, yields free iodine.

(3) If it is treated with ferrous sulphate, and subsequently with alkali and ferric salt, the mixture on acidification gives Prussian-blue, but contains no cyanate.

(4) The bromide, if mixed first with sodium sulphite and then with alkali, contains sulphate and cyanide; no cyanate is present.

(5) A moderately concentrated solution of cyanogen bromide, mixed with carbamide, effervesces on the addition of alkali hydroxide, nitrogen being evolved; hypobromite therefore appears to be present. The mixture in this case contains not only cyanide but also some cyanate.

In cases (2) to (5) mentioned above, if the addition of the alkali hydroxide precedes that of the various reducing agents named, no reduction occurs. A direct experiment showed that hypobromite instantly converts potassium cyanide into the cyanate.

With very dilute solutions of carbamide no effervescence occurs, cyanate, but no cyanide, being formed; even with highly concentrated solutions, however, some cyanate is detectable. These phenomena are explained by the fact that carbamide tends to give derivatives in which the haloid element is joined to nitrogen (Chattaway, *Proc. Roy. Soc.*, 1908, *A*, **81**, 381; T., 1901, **79**, 274); and since these behave as oxidising agents, the carbamide in such dilute solutions plays merely the part of a bromine-carrier; thus, when potassium cyanide (1 gram-molecule per litre) is oxidised by alkaline hypobromite (0·2 gram-molecule per litre), the volume-relations are unaffected by the previous addition of 1 molecule of carbamide for each molecule of cyanide present; but with hypobromite at five times the above concentration nitrogen escapes, and the proportion of hypobromite required to complete the oxidation is considerably greater than in the absence of the carbamide.

In all the above reactions the positive ion, joining the cyanogen, is eliminated as cyanide, the bromine being absorbed by the remainder of the molecule. The fact that water is non-ionised suffices to explain why it has no action on cyanogen bromide.

According to Chattaway and Wadmore (*loc. cit.*) hydrogen sulphide reacts quantitatively with cyanogen bromide, as shown by the equation:

$$CN{\cdot}Br + H_2S = HCN + HBr + S;$$

"a little" thiocyanic acid, however, being produced, the formation of which is attributed to the action of the sulphur on the hydrogen cyanide.

Our experimental results were as follows: A 2 per cent. solution of hydrogen cyanide, when shaken or gently warmed with flowers of sulphur, yielded with ferric chloride no red coloration; in presence of hydrogen bromide the same negative result was obtained. Various methods were tried of precipitating sulphur in solutions containing hydrogen cyanide or potassium cyanide acidified with hydrochloric acid; in no case (provided that the cyanide solution was kept acid) could any trace of thiocyanic acid be detected. Moreover, cyanogen bromide, when treated with potassium xanthate, yielded cyanide and a precipitate of sulphur, but no thiocyanic acid was found in the resultant mixture.

In order to determine the relative amount of thiocyanic acid produced in the reaction between cyanogen bromide and hydrogen sulphide, a dilute aqueous solution of the former was exactly saturated with a dilute solution of the latter; after removal of the sulphur by filtration, the thiocyanic acid contained in the clear liquor was determined by Barnes and Liddle's method; it was thus found that almost exactly one-half (0·505) of the cyanogen engaged had gone to form thiocyanic acid.

Since cyanogen bromide is not ionised by water or by dilute acids, it is natural to suppose that its chemical changes are brought about through union with the ionised fractions of the material presented, this union being followed by decomposition of the resultant additive compound. In many cases that material cannot develop the higher valence of the nitrogen atom, whilst the carbon atom has available two valencies, through which this combination can take place; for example, the reaction with alkali hydroxide is represented thus:

$$K_2O + {:}C{:}NBr \longrightarrow OK{\cdot}CK{:}NBr \longrightarrow KBrO + KCN \longrightarrow KBr + KCNO$$

(no regard is here paid to the molecular structures of the products).

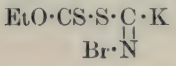
The reaction with sodium sulphite is similarly explained:

$$NaO{\cdot}SO{\cdot}O{\cdot}CNa{:}NBr \longrightarrow NaCN + SO(ONa){\cdot}OBr \longrightarrow NaCN + NaBr + SO_3.$$

In the case of hydriodic acid:

$$CHI{:}NBr \longrightarrow HCN + IBr \text{ and } IBr + HI = HBr + I_2;$$

with potassium xanthate:



$$\begin{array}{l} EtO{\cdot}CS{\cdot}S{\cdot}C{\cdot}K \\ \qquad\;\; Br{\cdot}N \end{array} \longrightarrow KCN + EtO{\cdot}CS{\cdot}SBr \text{ and}$$

$$EtO{\cdot}CS{\cdot}SBr + H_2O = EtO{\cdot}CS{\cdot}OH + HSBr \longrightarrow HBr + S.$$

More difficult to explain is the reaction between cyanogen bromide and hydrogen sulphide, for $HS{\cdot}CH{:}NBr$ would yield $HCN + HSBr$ instead of $HSCN + HBr$; moreover, Gutmann has shown (*Ber.*, 1909, **42**, 3628) that when alkali sulphide is used the reaction proceeds in accordance with the equation:

$$K_2S + CNBr = KBr + KSCN.$$

From analogy to the alkali oxide reaction the primary change in the case of alkali sulphide is:

$$K_2S + CN{\cdot}Br = CK({:}NBr){\cdot}SK \longrightarrow KCN + KSBr;$$

then:

$$CNK + BrSK = KBr + CNSK,$$

just as

$$CNK + BrOK = KBr + CNOK.$$

That potassium thiohypobromite is really produced and then desulphurised, as shown in these equations, receives support from the following facts.

(*a*) Alkaline solution of potassium sulphide, when mixed with potassium cyanide followed by acid, gives no reaction for thiocyanic acid.

(*b*) Potassium cyanide, mixed first with excess of alkaline hypobromite, next with alkaline sulphide, and then acidified, yields a liquid containing no thiocyanic acid (in other words, cyanate is not changed by alkali sulphide into thiocyanate).

(*c*) The mixture of cyanide and sulphide, if treated with alkaline hypobromite and then acidified, reacts copiously for thiocyanic acid.

These facts may be interpreted as follows: alkali sulphide acting on the hypobromite thus:

$$KBrO + KSH = KOH + KBrS;$$

the resultant thiohypobromite now transforms the cyanide into thiocyanate.

In the case of hydrogen sulphide it is possible that free thiohypobromous acid is first liberated, a portion of which decomposes forthwith, for sulphur is quickly (although not instantaneously) precipitated. Here the mechanism of the change is represented as follows:

$$CH(\colon NBr)\cdot SH \longrightarrow HCN + HSBr,$$

the resultant thiohypobromous acid being desulphurised by the hydrogen cyanide. Since the former, however, if produced at all, very soon decomposes, the hydrogen cyanide, unless able to seize at once the whole of the available sulphur, must undergo more or less incomplete transformation into thiocyanic acid.

Consistent with this view is the fact that the presence of hydrochloric acid serves to inhibit the production of thiocyanic acid. If thiohypobromous acid is analogous to hypobromous acid, its decomposition must be accelerated by concentrated hydrochloric acid, with consequent diminution in the amount of available sulphur.

Conversely, whatever delays the decomposition of the thiohypobromous acid or accelerates the rate at which the cyanide can desulphurise it, favours the production of thiocyanic acid; alkali may act in either or both of these ways.

When aqueous hydrogen sulphide is used, the large bulk required tends to produce ultimately solutions of almost equal concentration; at the commencement of mixing, however, this is not the case; we have found that the variation in the amount of thiocyanic acid formed at different concentrations of the cyanogen bromide is quite readily appreciable.

Since the products of the change are hydrobromic acid, thiocyanic acid, hydrogen cyanide, and sulphur, alkalimetric determination of the total number of equivalents of acid formed from a known quantity of cyanogen bromide measures the amount of thiocyanic acid present in the mixture. This was checked by independent measurements of the total acidity from 2 molecules of bromide (with $N/10$-alkali and methyl-orange), and of the thiocyanic acid (by Barnes and Liddle's method), the result, by calculation from the total acidity, and by direct determination, showing a difference of 0·05 equivalent in the amount of thiocyanic acid.

In the experiment previously mentioned (p. 975), the cyanogen bromide being very dilute, for 2 molecules taken, 1·01 equivalents of thiocyanic acid were found present; in the latter ones, for the same amount of bromide (used at concentrations from one-tenth to five-tenths of a gram-molecule per litre), the corresponding figures for the thiocyanic acid varied from 0·85 to 0·59 equivalent. To observe further the effect of concentration, excess of gaseous hydrogen sulphide was brought into contact with a solution of cyanogen bromide, containing 1·2 decigram-molecules per litre; reckoned as before, the amount of thiocyanic acid was now 0·43 equivalent. From the results obtained it appears that the proportion of thiocyanic acid is highly variable.

### *Sodium Thiosulphate and Cyanogen Bromide.*

When cold neutral aqueous solutions were mixed, alkalinity was developed, lasting for one or two minutes; the final products were hydrogen cyanide, alkali sulphate, bromide, tetrathionate, thiocyanate, and sulphite.

The alkalinity is due to the production of alkali cyanide:

$$NaO{\cdot}SO_2{\cdot}SNa + CN{\cdot}Br \longrightarrow NaO{\cdot}SO_2{\cdot}S{\cdot}CNa{\vdots}NBr \longrightarrow NaCN + NaO{\cdot}SO_2{\cdot}SBr;$$

then:

$$NaO{\cdot}SO_2{\cdot}SBr + NaS{\cdot}SO_2{\cdot}ONa = NaBr + Na_2S_4O_6.$$

Next, the alkali cyanide reacts with the tetrathionate (see Marshall, T., 1908, **93**, 1729), producing hydrogen cyanide, together with alkali sulphate, sulphite, and thiocyanate, the complete interaction being expressed by the equation:

$$4CN{\cdot}Br + 8Na_2S_2O_3 + H_2O = Na_2SO_4 + Na_2SO_3 + 2NaSCN + 2HCN + 3Na_2S_4O_6 + 4NaBr.$$

This was verified by the observations (i) that about one-half of the cyanogen in a known amount of the bromide went to form thiocyanate, and (ii) that when cyanogen bromide was treated with $N/10$-sodium thiosulphate, followed by $N/10$-iodine, the apparent molecular ratio of cyanogen bromide to thiosulphate consumed was 2:3; thus, four molecules of bromide absorb eight molecules of thiosulphate; but as the resultant mixture contains 1 molecule of sulphite, equivalent, so far as iodine-absorption is concerned, to two of thiosulphate, the apparent ratio of 4:6 is explained.

### *Thiocarbamide in Aqueous Solution, and Cyanogen Bromide.*

If these are mixed in presence of sodium hydrogen carbonate (which has no action on the bromide) carbon dioxide escapes; the resultant solution contains sodium thiocyanate, sodium bromide, and cyanamide, but no cyanide:

$$CSN_2H_4 + CN{\cdot}Br = HBr + HSCN + NH_2{\cdot}CN.$$

If, instead of the bicarbonate, a strong acid be present, the products consist solely of hydrocyanic acid, hydrobromic acid, and a salt of formamidine disulphide, together with a trace of sulphuric acid.

When the components are mixed in simple aqueous solution all the products named above are formed.

According to a recent hypothesis (Dixon and Taylor, T., 1912, **101**, 2502) it is supposed that in certain reactions of thiocarbamide the production of *iso*thiocarbamide derivatives is brought about by the primary formation of additive compounds, resulting through the development of quadrivalence on the part of the sulphur atom, and the subsequent decomposition of the substances thus produced; for example:

$$SC(NH_2)_2 + AcCl = AcSCl{:}C(NH_2)_2 = HCl + AcS{\cdot}C({:}NH){\cdot}NH_2.$$

A strongly ionised acid, HX, could, in like manner, become united with the sulphur atom to yield a compound, $C(NH_2)_2{:}SHX$, readily transformable into the basic form, $NH_2{\cdot}C(NH){\cdot}SH$, unstable by itself, but capable of retaining this configuration so long as it remains associated with a strong acid; and whilst the molecule is in this condition an oxidising agent, incapable of attacking the comparatively stable amino-group, could attack the SH-hydrogen. On the withdrawal of the combined acid the hydrogen at the ·SH-group, migrating, like an acyl radicle, to the imidic nitrogen, thiocarbamide would be regenerated.

There is reason to believe that such reversion occurs; for, in the reaction with cyanogen bromide, if the acidified solution of thiocarbamide is neutralised with sodium hydrogen carbonate, and then treated with the bromide, the products are the same as when the preliminary treatment with acid is omitted.

The mechanism of these reactions is explained as follows: where no acid is present, or allowed to become free, the thiocarbamide unites primarily with the whole molecule of cyanogen bromide; the elimination of the elements of hydrogen bromide from $(NH_2)_2C{:}S{:}CN{\cdot}Br$ produces $NH_2{\cdot}C({:}NH){\cdot}S{\cdot}CN$, the residue decomposing (like certain alkyl*iso*thiocarbamides) into cyanamide and thiocyanic acid (thiocyanic acid or cyanogen hydrogen sulphide being the analogue of alkyl hydrogen sulphide).

When the interaction takes place in presence of a strong acid the primary union between the *iso*thiocarbamide salt and the cyanogen bromide (as in the case of hydrogen sulphide) occurs at the ·SH-group, with formation of $NH_2{\cdot}C(NH){\cdot}C{\cdot}S{\cdot}CH{:}NBr$. This decomposes into hydrogen cyanide and $NH_2{\cdot}C(NH){\cdot}S{\cdot}Br$, the latter of which, attacking another molecule of *iso*thiocarbamide salt, yields hydrogen bromide and formamidine disulphide:

$$NH_2\cdot C(\colon NH)\cdot SH + BrS\cdot C(\colon NH)\cdot NH_2 = NH_2\cdot C(\colon NH)\cdot S\cdot S\cdot C(\colon NH)\cdot NH_2 + HBr;$$

thus, the non-production of thiocyanic acid is accounted for, as well as the production of all the substances detected in the reaction, save the trace of sulphuric acid. This last, no doubt, proceeds from the formamidine disulphide, which, as Werner has shown (T., 1912, **101**, 2182), is very easily oxidised.

The reaction with thiocarbamide in presence of acid is essentially parallel to that with cyanogen bromide and thiosulphate already mentioned. At all events, the explanation is similar for both; in each case an additive compound is formed; both decompose, giving cyanide and an unstable residue containing ·SBr; and in each case that residue combines with another molecule of the original thio-compound, eliminating hydrogen (or sodium) bromide.

The results when the interaction takes place in simple aqueous solution are now easily interpreted. At first, cyanamide is formed, together with hydrobromic and thiocyanic acids; these, combining with the yet unchanged thiocarbamide, and so producing *iso*thiocarbamide salt, render possible the formation of hydrogen cyanide and formamidine disulphide.

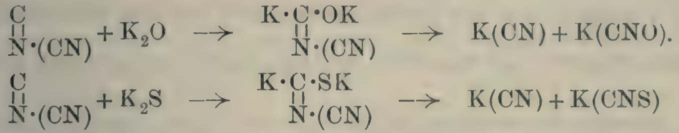
### *The Constitution of Cyanogen.*

To cyanogen the constitution usually assigned is $N\vdots C\cdot C\vdots N$, the chief grounds for this formula being that the substance is producible from oxamide or from glyoxime, and that, when treated with hydrochloric acid, it yields oxamide.

On the other hand, when passed into cold aqueous alkali hydroxide it decomposes, forming alkali cyanide and alkali cyanate; in ordinary circumstances such behaviour would be used as an argument to show that the two carbon atoms are not singly linked. Moreover, when kept in aqueous solution, cyanogen yields not merely oxalic acid, but also hydrocyanic acid and ammonium carbonate; it may be recalled, too, that hydrocyanic acid, under the same conditions, yields some oxalic acid.

Further, although the methods of formation named above are consistent with the view that cyanogen is a normal, rather than an *iso*-compound, other methods of preparation are known, which do not suggest a normal constitution for the product; for example, silver cyanide or mercuric cyanide when heated yields cyanogen; there is considerable reason to believe that these are *iso*cyanides, and hence (unless transformation is effected by the heating) the constitution of the resultant molecule is quite as likely to be $\colon C\colon N\cdot N\colon C\colon$ as to be $N\vdots C\cdot C\vdots N$. Besides, the compound is producible without strong heating, namely, through the decomposition of cupric *iso*cyanide. It may, perhaps, be objected that it is not certain that the cupric salt is an *iso*cyanide; but cyanogen bromide (which certainly is not $\mathrm{Br\cdot C\vdots N}$), when treated with cold aqueous potassium cyanide (probably $\mathrm{K\cdot N\colon C\colon}$), is said to yield ordinary cyanogen.

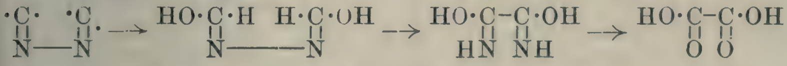
Further, the reaction with alkali hydroxide or with alkali sulphide so closely resembles that of cyanogen bromide with the same materials as to suggest that, in the case of cyanogen itself, one cyanogen radicle plays towards the other the same part as the halogen radicle in the bromide; in which case the changes may be explained on precisely similar lines, thus:



$$\begin{array}{l}\mathrm{C}\\ \|\\ \mathrm{N\cdot(CN)}\end{array} + \mathrm{K_2O} \longrightarrow \begin{array}{l}\mathrm{K\cdot C\cdot OK}\\ \quad\;\|\\ \quad\;\mathrm{N\cdot(CN)}\end{array} \longrightarrow \mathrm{K(CN)+K(CNO)}.$$

$$\begin{array}{l}\mathrm{C}\\ \|\\ \mathrm{N\cdot(CN)}\end{array} + \mathrm{K_2S} \longrightarrow \begin{array}{l}\mathrm{K\cdot C\cdot SK}\\ \quad\;\|\\ \quad\;\mathrm{N\cdot(CN)}\end{array} \longrightarrow \mathrm{K(CN)+K(CNS)}$$

There is no special difficulty in accounting for the slow production of oxalic acid (or oxamide) from aqueous cyanogen, supposing it to be an *iso*-compound:

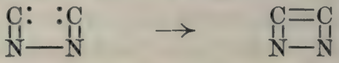


$$\begin{array}{c}\mathrm{\cdot C\cdot \quad \cdot C\cdot}\\ \|\qquad\;\|\\ \mathrm{N{-}{-}N}\end{array} \longrightarrow \begin{array}{c}\mathrm{HO\cdot C\cdot H \quad H\cdot C\cdot OH}\\ \|\qquad\qquad\quad\|\\ \mathrm{N{-}{-}{-}{-}N}\end{array} \longrightarrow \begin{array}{c}\mathrm{HO\cdot C{-}C\cdot OH}\\ \|\quad\|\\ \mathrm{HN\;\;NH}\end{array} \longrightarrow \begin{array}{c}\mathrm{HO\cdot C{-}C\cdot OH}\\ \|\quad\|\\ \mathrm{O\;\;\;O}\end{array}$$

or for that of hydrocyanic acid and ammonium carbonate, for here water (of course, very slowly) may behave like alkali hydroxide (see above), the resultant cyanic acid decomposing into ammonia and carbon dioxide.

Another point seems worth notice. By the dehydration of an amide of the type $\mathrm{R\cdot CO\cdot NH_2}$, the system $\mathrm{R\cdot C}\!\lessdot_{\mathrm{N:}}$ presumably occurs; here the free valencies, if they are to link up, must necessarily do so between the carbon and the nitrogen; the product, therefore (apart from molecular rearrangement), must be $\mathrm{R\cdot C\vdots N}$. In the dehydration of oxamide, however, this condition no longer holds; if two molecules of water are eliminated, the residue for the moment is $\begin{array}{l}\mathrm{:C\cdot N:}\\ \;\;|\\ \mathrm{:C\cdot N:}\end{array}$; so that—unless it be assumed that the carbon valencies are incapable of uniting with one another—the system $\begin{array}{l}\mathrm{C\colon N}\\ \|\;\;|\\ \mathrm{C\colon N}\end{array}$ would represent that proceeding from the most equable distribution of the four pairs of temporarily free valencies. Such a compound, breaking, according to circumstances, either at the doubly-linked carbon or at the singly-linked nitrogen pair of atoms, could yield all the products directly obtainable from cyanogen; thus, alkali hydroxide, by rupturing the double bond, could yield those compounds the genesis of which is not easily intelligible on the assumption that the carbon atoms are but singly linked; whilst hydrochloric acid, attacking preferably the nitrogen atoms, might readily cause a hydrolysis which would leave the carbon atoms in single linking.

This formula, too, meets to some extent at least the difficulty as to the production of ordinary cyanogen from *iso*cyanogen radicles; for, by the union of the two pairs of unsaturated carbon valencies, a cyclic compound could originate:



The constitution here suggested as best according with the properties of cyanogen is so far similar to that of Gutmann for cyanogen bromide, namely, $\overset{\mathrm{C}}{\underset{\mathrm{N}}{\|}}\!>\mathrm{Br}$, that, in the former, a tervalent group (CN) replaces the tervalent halogen of the latter, thus: $\overset{\mathrm{C}}{\underset{\mathrm{N}}{\|}}\!>(\mathrm{CN})$. Chattaway and Wadmore's formula for cyanogen bromide does not really conflict with that of Gutmann (*loc. cit.*), for the feeble extra valencies of the tervalent haloid element would very readily be broken, the carbon valencies thus becoming "free," and hence able to manifest the unsaturated character peculiar to the molecule, including its poisonousness. In like manner the cyanogen molecule, assisted, perhaps, by its own internal strains, could easily open out into a compound, $\dot{}\!:\!\mathrm{C}\!:\!\mathrm{N}\cdot\mathrm{N}\!:\!\mathrm{C}\!:$, the poisonousness of which might well be anticipated.

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## CII.—*Derivatives of* o-*Xylene. Part III. The Presence of a Mobile Nitro-group in Each of the Two Trinitro-*o-*xylenes.*

By Arthur William Crossley and Walter Ryley Pratt.

In a paper communicated to the Society in 1911 (T., **99**, 2345) reference was made to the action of alcoholic ammonia on the trinitro-*o*-xylenes, when a nitro-group is replaced by an amino-group, as reduction. In the discussion which followed the reading of the paper, Prof. Morgan (P., 1911, **27**, 308) pointed out that this was not reduction in the accepted sense of the word, but probably a simple replacement of a mobile nitro-group, and shortly afterwards Prof. Meldola called the attention of the authors to the same point, instancing the behaviour of 2 : 3 : 5-trinitro-4-acetylaminophenol (T., 1908, **93**, 1659) under similar conditions.

Further investigation has proved that such is, as a matter of fact, the case, a nitro-group in each of the two trinitro-*o*-xylenes being replaced readily, not only by the amino-group, but by a variety of substituted amino-groups. The reactions take place with liberation of nitrous acid, as exemplified by the following expression:

$$X\cdot NO_2 + NH_3 = X\cdot NH_2 + HNO_2.$$

The odour of nitrous acid was noticeable on evaporation of many of the reaction solutions, and, in one case, the interaction of 3 : 4 : 6-trinitro-*o*-xylene and benzylamine, crystals of benzylamine nitrite were actually isolated.

Derivatives have been prepared using the following primary amines: methylamine, ethylamine, aniline, *p*-toluidine, *o*- and *p*-anisidine, benzylamine, and with the secondary amines, dimethylamine and piperidine.

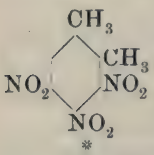
Neither 3 : 4 : 5-trinitro- nor 3 : 4 : 6-trinitro-*o*-xylene reacts with *o*- or *m*-nitroaniline or methylaniline, and although interaction takes place between both trinitro-*o*-xylenes and (*a*) diethylamine, (*b*) *p*-phenylenediamine with formation of deep coloured solutions and resinous products, no crystalline substances could be isolated. The same remark applies to 3 : 4 : 5-trinitro-*o*-xylene and *o*-toluidine, but from the latter substance and 3 : 4 : 6-trinitro-*o*-xylene a small amount of crystals was isolated, melting at 139°.

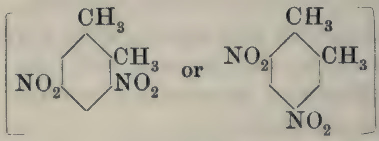
As pointed out by Meldola (*ibid.*, p. 1667), the influence of an ortho-substituent in these reactions is noted in the relative non-activity of *o*-nitroaniline and *o*-toluidine, although *o*-anisidine is decidedly reactive; but whereas Meldola obtained products with *m*-nitroaniline, this substance, as stated above, has been found to give negative results with the trinitro-*o*-xylenes.

The reactions were, as a rule, carried out by adding slightly more than the calculated amount of the amine to a cold alcoholic suspension of the trinitro-*o*-xylene, and allowing the mixture to remain. In other cases the solution was heated for lengths of time varying from ten minutes to three hours, and solvents other than alcohol, for example, ether and benzene, were employed. The excess of amine was, in most cases, removed by washing with dilute hydrochloric acid, in which solvent the amino-products are practically insoluble.

There are marked differences in the rates at which the various reactions take place as indicated in some cases in the experimental portion of this paper; for example, 3 : 5-dinitro-4-benzylamino-*o*-xylene is formed almost immediately on adding benzylamine to 3 : 4 : 5-trinitro-*o*-xylene, although the latter is only suspended in alcohol, whereas the reaction with aniline, under similar conditions, is not complete in fourteen days. Many experimental difficulties will, however, have to be overcome before any quantitative measurements of value can be given, and in many cases the difficulties appear to be insurmountable.

The constitutions of the two trinitro-*o*-xylenes are represented by formulæ I and II, and there can be no doubt as to which of the nitro-groups is the active one (marked *) in each case, for when the products of the action of ammonia on these substances are diazotised and the diazo-group removed by boiling with alcohol, they both yield 3 : 5-(4 : 6)dinitro-*o*-xylene (III).


(I.)



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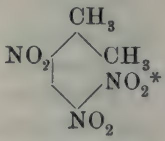
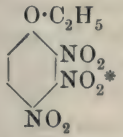
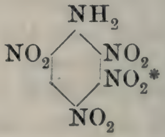

(II.)

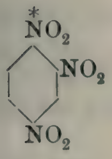
It would appear to be an established fact that in order to exhibit mobility a nitro-group must be situated in an ortho-position, and in certain cases also para- with respect to some acid radicle present in the nucleus (compare Hepp, *Annalen*, 1882, **215**, 362, 364; Staedel and Kolb, *ibid.*, 1890, **259**, 208, 220, 224; Laubenheimer, *Ber.*, 1876, **9**, 1826, 1828; 1878, **11**, 1156, 1159; Nietzki, *Ber.*, 1878, **11**, 1448; Flürscheim, P., 1910, **26**, 81; Meldola and Eyre, T., 1901, **79**, 1076; 1902, **81**, 988; Meldola, T., 1906, **89**, 1935; 1908, **93**, 1659; Blanksma, *Rec. trav. chim.*, 1908, **27**, 42, 49).

In 3 : 4 : 5-trinitro-*o*-xylene the mobile group is ortho with regard to two other nitro-groups, corresponding exactly with the position of the active group (marked *) in 2 : 3 : 4-trinitrophenetole (IV) (Blanksma, *loc. cit.*, p. 50), and also in tetranitroaniline (V) (Flürscheim):

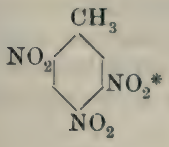

(IV.)


(V.)

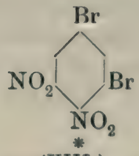
In 2 : 4 : 6-trinitro-*o*-xylene the mobile group is situated ortho and para to the other acidic groups, a position which seems perhaps to be the most favourable for the change to take place, as evidenced by trinitrobenzene (VI); trinitrotoluene (VII) (Hepp, *loc. cit.*, 361, 364); tetranitroaniline (V) (Flürscheim); and dibromodinitrobenzene (VIII) (Blanksma, *loc. cit.*, 43):



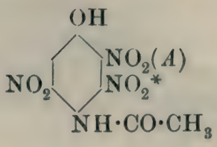
(VI.)



(VII.)



(VIII.)



(IX.)

It is, however, of interest to note that although Meldola's trinitroacetylaminophenol (IX) contains a nitro-group (*A*) situated ortho and para to two other nitro-groups, it is not this group but the one in position 3 (*) which is mobile. Evidently in this case mobility must be to some extent influenced by the other groups present in the molecule.[†]

As other derivatives of *o*-xylene have been encountered which appear to contain mobile groups, the investigation is being continued more particularly with regard to the relative rates at which the mobile nitro-groups are replaced.

## EXPERIMENTAL.

### *Derivatives of* 3 : 4 : 5-*Trinitro*-o-*xylene.*

### 3 : 5-*Dinitro*-o-4-*xylidine* (3 : 5-*dinitro*-4-*amino*-o-*xylene*) (T., 1911, **99**, 2350).

3 : 5-*Dinitro*-4-*methylamino*-o-*xylene*, prepared from methylamine and trinitro-*o*-xylene in alcoholic solution in the cold, crystallises from alcohol, in which solvent it is very sparingly soluble, in stout, scarlet plates, melting at 143° :

0·1058 gave 16·8 c.c. $N_2$ (moist) at 17° and 759 mm. N = 18·67.

$C_9H_{11}O_4N_3$ requires N = 18·66 per cent.

3 : 5-*Dinitro*-4-*dimethylamino*-o-*xylene* is obtained, in nearly theoretical amount, by heating the trinitro-*o*-xylene for ten minutes with dimethylamine in alcoholic solution. It crystallises from alcohol in orange-red needles, melting at 103—104° :

0·1104 gave 16·6 c.c. $N_2$ (moist) at 16° and 762 mm. N = 17·81.

$C_{10}H_{13}O_4N_3$ requires N = 17·57 per cent.

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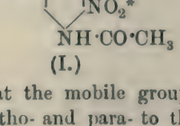
[†] Since the above paper was written, Professor Meldola has kindly communicated to the authors that further work has shown that the trinitroacetylaminophenol described by him has the nitro-groups in the 2 : 3 : 6-positions and not 2 : 3 : 5-, as previously stated (compare T., 1913, **103**, 877). The latter substance has recently been prepared and will shortly be described :



(I.)

It will, therefore, be noted that the mobile group in 2 : 3 : 6-trinitroacetylaminophenol (I) is again situated ortho- and para- to the other two nitro-groups in the molecule.

3 : 5-*Dinitro*-4-*ethylamino*-o-*xylene*, prepared by heating trinitro-*o*-xylene with excess of ethylamine in alcoholic solution for three hours (yield almost theoretical), is readily soluble in chloroform or benzene, and crystallises from alcohol in orange needles, melting at 115° :

0·1536 gave 23·2 c.c. $N_2$ (moist) at 14° and 748 mm. N = 17·69.

$C_{10}H_{13}O_4N_3$ requires N = 17·57 per cent.

3 : 5-*Dinitro*-4-*anilino*-o-*xylene*.—Trinitro-*o*-xylene was suspended in alcohol, and excess of aniline added, when, on standing, the nitro-compound slowly passed into solution, and red crystals separated. The reaction was not, however, ended after fourteen days, but in ethereal solution it was complete in three days. Dinitroanilinoxylene crystallises from alcohol in orange-red needles, melting at 134° :

0·1318 gave 16 c.c. $N_2$ (moist) at 15° and 770 mm. N = 14·58.

$C_{14}H_{13}O_4N_3$ requires N = 14·63 per cent.

3 : 5-*Dinitro*-4-p-*toluidino*-o-*xylene* was prepared from the trinitro-*o*-xylene and *p*-toluidine in alcoholic solution on gentle warming. Prolonged heating causes the formation of large quantities of resinous substances. It crystallises from alcohol in fine, orange needles, melting at 133° :

0·1120 gave 13·2 c.c. $N_2$ (moist) at 10° and 766 mm. N = 13·98.

$C_{15}H_{15}O_4N_3$ requires N = 13·99 per cent.

3 : 5-*Dinitro*-4-o-*anisidino*-o-*xylene* is obtained, in theoretical amount, by allowing trinitroxylene and *o*-anisidine to remain in alcoholic solution for seven days. It crystallises from alcohol in stout, crimson-lake needles, melting at 138—139° :

0·1500 gave 16·8 c.c. $N_2$ (moist) at 10° and 753 mm. N = 13·38.

$C_{15}H_{15}O_5N_3$ requires N = 13·24 per cent.

3 : 5-*Dinitro*-4-p-*anisidino*-o-*xylene* crystallises from alcohol in bright crimson needles, melting at 131° :

0·1454 gave 16·6 c.c. $N_2$ (moist) at 19° and 762 mm. N = 13·38.

$C_{15}H_{15}O_5N_3$ requires N = 13·24 per cent.

The reaction with *p*-anisidine is complete in three days in ethereal solution.

3 : 5-*Dinitro*-4-*benzylamino*-o-*xylene* is formed in almost theoretical quantity in a very short time after adding excess of benzylamine to an alcoholic suspension of trinitro-*o*-xylene. It is readily soluble in ether, chloroform, benzene, or acetone, but only sparingly so in alcohol, from which solvent it crystallises in glistening, orange plates, melting at 128·5° :

0·1164 gave 13·6 c.c. $N_2$ (moist) at 17° and 775 mm. N = 14·07.

$C_{15}H_{15}O_4N_3$ requires N = 13·99 per cent.

3 : 5-*Dinitro*-4-*piperidino*-o-*xylene* is obtained in 90 per cent. of

the theoretical amount by heating the trinitro-*o*-xylene with excess of piperidine for two hours in benzene solution. It crystallises from alcohol in bright, orange-red needles, melting at 137—138°:

0·1139 gave 14·8 c.c. $N_2$ (moist) at 16° and 752 mm. N = 15·18.

$C_{13}H_{17}O_4N_3$ requires N = 15·05 per cent.

### *Derivatives of* 3 : 4 :-6-*Trinitro*-o-*xylene.*

### 4 : 6-*Dinitro*-o-3-*xylidine* (4 : 6-*dinitro*-3-*amino*-o-*xylene*, T., 1911, **99**, 2348).

4 : 6-*Dinitro*-3-*methylamino*-o-*xylene* is prepared by suspending trinitro-*o*-xylene in alcohol and adding excess of a 30 per cent. solution of methylamine in alcohol. A green colour is first produced, changing to blue, red, and finally yellow, with deposition of yellow crystals (theoretical amount). It crystallises from alcohol in orange needles, melting at 90—91°:

0·0941 gave 15·5 c.c. $N_2$ (moist) at 20° and 755 mm. N = 18·96.

$C_9H_{11}O_4N_3$ requires N = 18·66 per cent.

4 : 6-*Dinitro*-3-*dimethylamino*-o-*xylene*.—On adding an alcoholic solution of dimethylamine to trinitroxylene suspended in alcohol, a green colour is immediately developed, which changes to blue, purple, red, and finally yellow, with deposition of solid. When the mixture is heated on a water-bath the yellow stage is reached in ten minutes. The solid crystallises from alcohol in orange needles, melting at 91—92°:

0·1074 gave 16·4 c.c. $N_2$ (moist) at 18° and 756 mm. N = 17·82.

$C_{10}H_{13}O_4N_3$ requires N = 17·57 per cent.

4 : 6-*Dinitro*-3-*ethylamino*-o-*xylene*.—When an alcoholic solution of ethylamine is added to a suspension of trinitro-*o*-xylene in alcohol, heat is evolved, a yellow colour developes, and a yellow solid is deposited (yield theoretical). It crystallises from alcohol in short, orange needles, melting at 75—76°:

0·1288 gave 19·4 c.c. $N_2$ (moist) at 15° and 748 mm. N = 17·57.

$C_{10}H_{13}O_4N_3$ requires N = 17·57 per cent.

4 : 6-*Dinitro*-3-*anilino*-o-*xylene*.—Trinitro-*o*-xylene is suspended in absolute alcohol, and three times the calculated quantity of aniline added. A red colour at once develops, and after forty-eight hours all the trinitro-compound disappears and is replaced by red plates. The reaction is accelerated by heat, but resinous substances are also formed, whereas by carrying it out in ether and evaporating the ether without the aid of heat, a theoretical amount of the substance is obtained.

Dinitroanilinoxylene is very soluble in chloroform, ether, benzene, or acetone, but only sparingly so in light petroleum, and crystallises from alcohol in bright red plates, melting at 137°:

0·1350 gave 17 c.c. $N_2$ (moist) at 16° and 758 mm. N = 14·79.
$C_{14}H_{13}O_4N_3$ requires N = 14·63 per cent.

4 : 6-*Dinitro*-3-p-*toluidino*-o-*xylene.*—Trinitroxylene, mixed with dry, powdered *p*-toluidine, develops a red colour, and a deep red solution is formed on addition of alcohol. After twelve hours a quantity of red crystals separate, representing 70 per cent. of the theoretical amount. The change takes place more rapidly on heating, but resinous substances are also formed.

Dinitro-*p*-toluidinoxylene crystallises from alcohol in orange-red plates, melting at 111°:

0·1316 gave 15·6 c.c. $N_2$ (moist) at 14° and 766 mm. N = 14·22.
$C_{15}H_{15}O_4N_3$ requires N = 13·99 per cent.

4 : 6-*Dinitro*-3-o-*anisidino*-o-*xylene*, prepared in alcoholic solution, crystallises from alcohol in brick-red needles, melting at 126—127°:

0·1645 gave 18·6 c.c. $N_2$ (moist) at 13° and 758 mm. N = 13·46.
$C_{15}H_{15}O_5N_3$ requires N = 13·24 per cent.

4 : 6-*Dinitro*-3-p-*anisidino*-o-*xylene* crystallises from alcohol in garnet-coloured, flattened needles, melting at 118°. The reaction between *p*-anisidine and trinitroxylene is complete in ethereal solution after forty-eight hours:

0·1356 gave 15·4 c.c. $N_2$ (moist) at 14° and 758 mm. N = 13·47.
$C_{15}H_{15}O_5N_3$ requires N = 13·24 per cent.

4 : 6-*Dinitro*-3-*benzylamino*-o-*xylene.*—When benzylamine is added to a benzene solution of trinitroxylene, a yellow colour is formed and heat evolved. On cooling, crystals of benzylamine nitrite separate. The whole is heated on a water-bath for three hours, and after working up in the usual way the resulting oil slowly solidifies. The solid is readily soluble in chloroform, benzene, or acetone, and crystallises from a mixture of chloroform and light petroleum (b. p. 40—60°) in orange prisms, melting at 59°:

0·1868 gave 22 c.c. $N_2$ (moist) at 16° and 763 mm. N = 13·97.
$C_{15}H_{15}O_4N_3$ requires N = 13·99 per cent.

4 : 6-*Dinitro*-3-*piperidino*-o-*xylene* crystallises from aqueous alcohol or aqueous acetone in orange plates, melting at 98°:

0·0938 gave 12·1 c.c. $N_2$ (moist) at 16° and 752 mm. N = 15·07.
$C_{13}H_{17}O_4N_3$ requires N = 15·05 per cent.

The reaction with piperidine is best carried out by heating in alcoholic solution for three hours.

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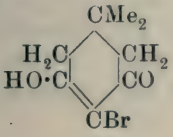
# CIII.—*Derivatives of o-Xylene. Part IV. Synthesis of 4 : 5-Dibromo-3-o-xylenol.*

By Arthur William Crossley and Sydney Smith.

In 1903 Crossley and Le Sueur (T., **83**, 127) described a dibromoxylenol melting at 96·5°, which was obtained from the product of the action of phosphorus pentabromide on dimethyldihydroresorcin. It was then suggested that this substance was a derivative of 3-*o*-xylenol, because on further bromination it yielded a tribromoxylenol melting at 183°—tribromo-3-*o*-xylenol melting at 184°. In the action of phosphorus pentabromide on dimethyldihydroresorcin, the main initial products are not bromoxylenols, but are hydroaromatic in nature, the principal one isolated being tribromodimethyl*cyclo*hexenone (tribromoketodimethyltetrahydrobenzene) (III or IV).

Dibromodimethyl*cyclo*hexenone (II) results from the action of phosphorus tribromide on bromodimethyldihydroresorcin (I) (*loc. cit.*, p. 122), and its constitution would therefore appear to be beyond doubt. When treated with bromine, it is converted into tribromodimethyl*cyclo*hexenone, which may be represented by either of the two formulæ III or IV, although the former appears to be the more likely.



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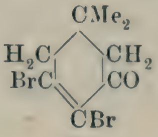

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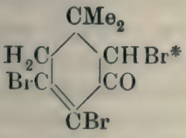

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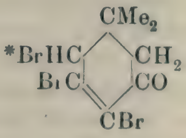
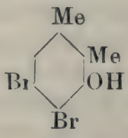


(IV.)

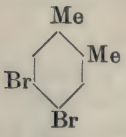
Recently (P., 1912, **28**, 333) the above-mentioned dibromoxylenol has been obtained by the action of dilute alcoholic potassium hydroxide on tribromodimethyl*cyclo*hexenone. In this reaction, (*a*) one bromine atom must be eliminated as hydrogen bromide, and this would almost certainly be the one marked *, in which case its actual position in tribromodimethyl*cyclo*hexenone is of no moment to the present argument, but if this is the bromine atom to be removed then the position of the remaining bromine atoms is fixed; (*b*) the ketonic group would become hydroxylic, thus determining the position of the hydroxyl group in the resulting dibromoxylenol; (*c*) a methyl group must wander, and since on further bromination the resulting dibromoxylenol has been proved to yield tribromo-3-*o*-xylenol, the positions of the methyl groups relative to the hydroxyl group become evident.

Assuming this argument to be correct, only one possibility exists for the constitution of the dibromoxylenol melting at 96·5°, namely, 4 : 5-dibromo-3-*o*-xylenol (V), and this supposition has now been proved to be correct by the synthesis of a substance of this constitution, which proves to be identical with the dibromoxylenol obtained by the action of phosphorus pentabromide on dimethyldihydroresorcin.



(V.)

Jacobson (*Ber.*, 1884, **17**, 2377) has shown that when *o*-xylene is brominated in the presence of iodine, two dibromo-*o*-xylenes are produced, the one a liquid, the other a solid, melting at 88°. That the latter is 4 : 5-dibromo-*o*-xylene (VI) was proved by the fact that on treatment with sodium and methyl iodide, it gave durene (1 : 2 : 4 : 5-tetramethylbenzene, VII). When 4 : 5-dibromo-*o*-xylene is nitrated, it yields a dibromonitro-*o*-xylene, and as the molecule is symmetrical, this can only be 4 : 5-dibromo-3-nitro-*o*-xylene (VIII), which on reduction is converted into 4 : 5-dibromo-3-amino-*o*-xylene (IX). In this latter substance the amino-group can be replaced by hydroxyl through the agency of the diazo-reaction, and there results 4 : 5-dibromo-3-*o*-xylenol.



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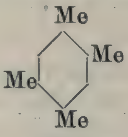

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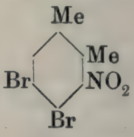

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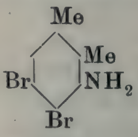

(IX.)

## EXPERIMENTAL.

4 : 5-Dibromo-*o*-xylene (Jacobson, *loc. cit.*) was prepared from quantities of 10 grams of *o*-xylene, 0·4 gram of iodine, and 31 grams of bromine. The whole, after dissolving in ether, washing with potassium hydroxide solution, water, drying and evaporating the ether, weighed 24—25 grams, and was semi-solid. The amount of

pure dibromo-*o*-xylene obtained after crystallisation from alcohol was 11·5 grams, melting at 87—88°.

Dibromo-*o*-xylene (compare Tohl, *Ber.*, 1885, **18**, 2562) in quantities of 10 grams was warmed on the water-bath for one hour, and frequently shaken with 25 c.c. of a mixture of 3 volumes of fuming nitric acid and 1 volume of glacial acetic acid. After pouring into water and recrystallising from alcohol, 8 grams of 4 : 5-dibromo-3-nitro-*o*-xylene, melting at 143—144°, were obtained.

Dibromonitro-*o*-xylene was reduced in quantities of 5 grams at one time by heating for four hours with 15 grams of iron filings and 50 grams of glacial acetic acid. After steam distillation and crystallisation of the resulting solid from alcohol, 2 to 2·4 grams of 4 : 5-dibromo-3-*o*-xylidine, melting at 103°, were isolated.

4 : 5-Dibromo-3-*o*-xylidine was diazotised by suspending 5 grams in 75 c.c. of 40 per cent. sulphuric acid, and, while maintaining the temperature at 50—60°, gradually adding a 20 per cent. solution of sodium nitrite until a reaction was shown to starch-iodide paper. The whole was then poured into 125 c.c. of 40 per cent. sulphuric acid, heated to near the boiling point, and after some time was distilled in a current of steam, when a white solid passed over. The distillate was rendered alkaline with sodium hydroxide, filtered from a slight amount of insoluble matter, acidified, and the precipitated dibromoxylenol crystallised from dilute alcohol (yield, 2·8 to 3·5 grams):

0·1230 gave 0·1663 AgBr. Br = 57·52.

$C_8H_8OBr_2$ requires Br = 57·14 per cent.

4 : 5-*Dibromo*-3-o-*xylenol* is insoluble in sodium carbonate solution, readily soluble in the cold in potassium hydroxide solution, chloroform, acetone, benzene, or ether, and crystallises from aqueous alcohol in long, glistening, flattened needles, melting at 97°. When treated with bromine in chloroform solution, it is converted into 4 : 5 : 6-tribromo-3-*o*-xylenol, melting at 185°.

The *acetyl* derivative was prepared by heating the xylenol with a mixture of acetyl chloride and acetic anhydride. It is readily soluble in the cold in acetone, ethyl acetate, chloroform, or benzene, somewhat less readily so in alcohol, and crystallises from light petroleum (b. p. 40—60°) in large, hexagonal prisms, melting at 78°:

0·1103 gave 0·1296 AgBr. Br = 49·99.

$C_{10}H_{10}O_2Br_2$ requires Br = 49·69 per cent.

The *benzoyl* derivative, prepared in the usual manner, crystallises from alcohol in small, transparent rhombs, melting at 153°:

0·1116 gave 0·1100 AgBr. Br = 41·93.

$C_{15}H_{12}O_2Br_2$ requires Br = 41·67 per cent.

It is readily soluble in the cold in chloroform, somewhat less so in cold ethyl acetate or benzene, and readily soluble in acetone on warming.

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# CIV.—*The Behaviour of Calcium and Magnesium Salts with Soap Solutions and the Determination of Hardness of Water.*

By Helen Masters and Henry Llewellyn Smith.

Many observers have noted the difference in behaviour of magnesium and calcium salts when titrating waters with soap solutions for the determination of "hardness," and the difficulty of obtaining a satisfactory end-point in the presence of magnesium salts has become well known.

The work described below was undertaken with the object of tracing the cause of this difference and determining more satisfactory conditions.

Buchner (*Chem. Zeit.*, 1892, **16**, 1854) states that temperature exerts a great influence on the appearance of the lather. The thick foam which remains five minutes after the precipitation of calcium and magnesium salts at 15° remains constant for hardly a minute at the higher temperatures reached in midsummer, and scarcely longer with a further addition of soap.

Teed (*J. Soc. Chem. Ind.*, 1889, **8**, 256) states that calcium salts require $1\frac{1}{3}$ and magnesium salts $1\frac{1}{2}$ times the equivalent of soap for the production of a permanent lather.

Winkler (*Zeitsch. anal. Chem.*, 1901, **40**, 82) states that magnesium salts require more soap than an equivalent amount of calcium salts, potassium oleate being the soap used.

Jackson (*Chem. News*, 1884, **49**, 149), using Castile soap solution, found that when the hardness due to calcium salts exceeded six degrees, no evidence could be obtained of magnesium salts unless present in amount exceeding 10 per cent. of the calcium salts. He suggested heating to 70° to obtain more accurate results.

The standard soap solutions used in the work here described were made from various soaps, and the results indicate that soaps made from the saturated fatty acids give more accurate results than those derived from unsaturated acids. As, however, sodium oleate makes a convenient and stable solution, its behaviour was further investigated. The solubility of calcium and magnesium oleates and the nature of the precipitate obtained on titration seemed worth investigating.

Standard solutions of calcium and magnesium salts were titrated with aqueous-alcoholic solutions of sodium oleate, potassium palmitate, Castile soap, and potassium myristate. The soap solutions (with the exception of Castile soap) were prepared by dissolving the acid in alcohol, neutralising with sodium or potassium hydroxides, and diluting with water and alcohol, so that the finished solution contained 50 per cent. of alcohol. They were standardised, so that 100 c.c. water containing 10 milligrams of calcium carbonate required 11 c.c. of soap solution.

The molecular weights of the acids were determined by titration with alkali in alcoholic solution. The iodine absorption was determined by means of Hanus' solution.

The following results were obtained:

Myristic acid, M.W. 228; iodine absorption, 0·5 per cent.; m. p. 53·3°.

Palmitic acid, M.W. 257·7; iodine absorption, 0·8 per cent.; m. p. 61·5—62°.

Oleic acid, M.W. 283; iodine absorption, 87·4 per cent., corresponding with 97 per cent. of oleic acid; the refractive index was 1·4542 at 40°.

The Castile soap gave a clear neutral solution in alcohol. The fatty acids had a mean molecular weight of 280·9, and melted at 23°. They absorbed 46·1 per cent. of iodine, corresponding with 52 per cent. of unsaturated acids in terms of oleic acid. Refractive index 1·4493 at 40°. As will be seen, a mixture of potassium myristate and sodium oleate standard solutions in equal volumes gives the same results as the solution of Castile soap when used to titrate calcium and magnesium salts.

All the titrations were done on 100 c.c. of water containing calcium or magnesium salts, separately or together, equivalent to 10 milligrams of calcium carbonate.

The figures on p. 994 are the mean of a large number of closely agreeing titrations.

Titrations with sodium oleate and magnesium salts were carried out at temperatures ranging from 15° to 60°, and the following results obtained. At temperatures up to 30°, 13 c.c. of sodium oleate were required, whilst above 40° only 8 c.c. were necessary. The change between these two temperatures seems somewhat sudden; at 35°, 11—12 c.c. were required. The difficulty of keeping the temperature constant while titrating and shaking, and of obtaining a sharp end-point, prevented a more accurate determination.

| | Equivalent (in milligrams of $CaCO_3$) of the salts contained in 100 c.c. of solution. | | C.c. of soap solution required | |
|---|---|---|---|---|
| Soap solution used. | $CaCl_2$. | $MgCl_2$. | at 15°. | at 60°. |
| Sodium oleate | 10 | — | 11·0 | 12—12·5 |
| | — | 10 | 13·0 | 8·0 |
| Potassium palmitate | 10 | — | 11·0 | 10—11 |
| | — | 10 | 11·0 | 9·0 |
| Castile soap | 10 | — | 11·0 | 12·0 |
| | — | 10 | 12·5 | 8·0 |
| Myristate and oleate | 10 | — | 11·0 | — |
| (equal volumes) | — | 10 | 12·5 | — |
| Potassium myristate | 10 | — | 11·0 | 10·5—11·0 |
| | — | 10 | 11·0 | 10·5—11·0 |

The results in the table given above show the difference in behaviour of soaps made from saturated and unsaturated fatty acids when used for titrating calcium and magnesium salts.

With palmitate and myristate, the end-point, whilst sharp at the ordinary temperature, became unsatisfactory at 60°.

The lather obtained from sodium oleate and calcium chloride was more lasting at 15° than at 60°, whilst with magnesium chloride a white froth was formed early at 60°, which made the true lather difficult to distinguish.

With water and sodium oleate alone, a more profuse lather was obtained at the higher temperature.

The potassium palmitate solution was unsatisfactory, as except in the warmest weather a considerable precipitate formed even after keeping for twenty-four hours and filtering. The precipitate, on analysis, proved to be potassium hydrogen palmitate. Increasing the quantity of alcohol to 75 per cent. prevented this to some extent, but not sufficiently to make it stable.

Potassium myristate gave a clear solution which was quite as stable as that of sodium oleate, and when standardised with calcium chloride gave accurate results with magnesium salts and with mixtures of calcium and magnesium salts in all proportions.

When potassium palmitate was used for titrating magnesium salts, it was noted that after the addition of about half the soap, the magnesium palmitate appeared as a flocculent precipitate suspended in a clear liquid. As the titration was completed this precipitate was rapidly dispersed, and at the end the liquid was uniformly cloudy, and no sedimentation took place until after some minutes. The same kind of separation took place when potassium myristate was used, but it was not so marked. With sodium oleate no such separation was noticed.

This observation is of interest as showing possibly some analogy to the coagulation of colloids by salts of metals of different valency, the magnesium sulphate having a greater effect than the sodium sulphate finally present.

With waters containing both calcium and magnesium salts, accurate results could only be obtained with soaps made from saturated fatty acids. With sodium oleate the end-points were unsatisfactory. When the calcium salts present exceeded 70 per cent. of the total hardness, and the titration was performed rapidly, a lather was obtained when rather more than the equivalent of the calcium alone was added. On keeping, the titration could be continued, but not with much accuracy, and the total amount of soap used was less than required by theory. This was the case at all temperatures with mixtures varying from 10 per cent. of magnesium and 90 per cent. of calcium to 90 per cent. of magnesium and 10 per cent. of calcium.

The equivalent of sodium oleate used in these experiments agrees closely with the figures given by Teed (*loc. cit.*).

One hundred c.c. of sodium oleate solution contained $Na_2O$ equivalent to 25 c.c. of $N/10$-hydrochloric acid, giving 0·760 sodium oleate in 100 c.c. of solution.

Ten milligrams of calcium carbonate (equivalent to 60·8 milligrams of sodium oleate) required 83·6 milligrams, or 1·37 times the equivalent of oleate.

An equivalent amount of magnesium salts required 98·8 milligrams of sodium oleate, or 1·62 times the equivalent.

It was noted, however, that at 60° the magnesium salts used up 60 milligrams only or practically the equivalent.

Some of the solutions titrated with sodium oleate were kept for some time. Those containing calcium salts remained translucent, with hardly any formation of precipitate, but on heating to 60° they became opaque, and particles separated. In the case of magnesium salts, an opaque mixture with considerable precipitate formed after a short time at 15°. On heating to 60°, the mixture did not clear, but the particles became suspended, and there was but little sediment. Attempts were made to separate this suspended matter by centrifugalising for fifteen to twenty minutes at 2,000 revolutions per minute. With calcium salts no separation occurred. With magnesium salts a fair separation was effected. Magnesium sulphate equivalent to 10 milligrams of calcium carbonate was used with 6 c.c. to 15 c.c. of sodium oleate solution in a total volume of 100 c.c. With 15 c.c. of oleate, but little separation occurred. In all cases the clearer supernatant liquid contained magnesium, and was alkaline to methyl-orange.

The precipitate from a number of experiments (using 10 c.c. of sodium oleate solution) was collected and dried in a vacuum over sulphuric acid, after pressing on a porous plate. Analysis showed it to be normal magnesium oleate with a small quantity of sodium salt. (Found, MgO = 6·46. Calc., MgO = 6·83 per cent.)

A few mixtures were placed in the centrifuge at 60—80°, but no separation occurred at this temperature.

In the case of titrations carried out with soaps obtained from saturated fatty acids, separation occurred with both calcium and magnesium salts on keeping.

From the behaviour of sodium oleate with calcium and magnesium salts, it appeared likely that the solubilities of the oleates had some influence on the results. They were determined at 15° and 60°, upward filtration being employed through a layer of filter paper and muslin over the end of a tube $\frac{3}{8}$ in. in diameter.

The salts were prepared by mixing excess of solutions of the chlorides with sodium oleate. They were purified by washing and drying in a vacuum over sulphuric acid, redissolving in light petroleum (in which they are freely soluble), filtering, and evaporating. Both salts were in a porous, granular condition, and tended to become moist and sticky on exposure to air, particularly the magnesium salt, which softens to a pasty mass in water above 40°.

These salts are not quite pure, some water and light petroleum finally remaining to the extent of about 5 per cent.

On analysis, the magnesium salt gave MgO = 6·4, and oleic acid = 91·65 per cent., or 1 : 14·13 (theory, 1 : 14·10). The calcium salt contained CaO = 8·87 (theory, 9·30), corresponding with 95·3 per cent. of calcium oleate.

The quantities dissolving in water are so small that it was only possible to estimate the calcium and magnesium oxides (weighed as pyrophosphate). About 150 grams of solution were taken for the estimation. At the higher temperature, 60°, it was found necessary to redissolve the calcium oxide obtained by ignition, and reprecipitate as oxalate, as an appreciable amount of soluble matter was obtained from the glass vessel. The solutions were slightly turbid even after filtration, and were faintly alkaline to phenolphthalein.

Calcium and magnesium palmitate were prepared by mixing excess of a solution of the chloride with a solution of potassium palmitate. The precipitate was thoroughly washed until, on digestion with water and filtering, the filtrate gave no reaction for chloride.

The following figures were obtained, 100 grams of solution being used in each case:

| Temperature. | Calcium oleate. | Magnesium oleate. | Calcium palmitate. | Magnesium palmitate. |
|---|---|---|---|---|
| 15° | 0·0041 CaO | 0·0015 MgO | 0·0030 CaO | 0·0009 MgO |
| 60 | 0·0023 CaO | 0·0020 MgO<br>to 0·0025 | 0·0032 CaO | 0·0010 MgO |

With both calcium and magnesium palmitate, temperature has no appreciable effect on the solubility, and neither solution gave a pink colour with phenolphthalein.

The solution of magnesium oleate in water at all temperatures gave a lather on shaking, like the false lather always obtained early in the titrations of magnesium salts.

That the separation of particles of magnesium oleate, previously mentioned, is the cause of more soap solution being required is shown by the following experiments. Magnesium oleate was added to 100 c.c. of water containing magnesium sulphate equivalent to 10 milligrams of calcium carbonate, and the mixture then titrated with sodium oleate solution:

| | |
|---|---|
| $MgSO_4$ alone ..................... | 13·0 c.c. sodium oleate required |
| $MgSO_4$ + 0·1 gram Mg oleate | 15·5 c.c. ,, ,, ,, |
| $MgSO_4$ + 0·2 grams Mg oleate | 17·0 c.c. ,, ,, ,, |

At temperatures above 40°, the addition of magnesium oleate did not increase the amount of soap solution necessary to form a lather, and when the mixture was kept above this temperature for some time before titrating, the amount of soap solution then required to form a lather was slightly less than that required by the magnesium sulphate alone.

Similar experiments with calcium salts gave results in the reverse order, the addition of calcium oleate at 15° affecting the result but little:

| | |
|---|---|
| $CaCl_2$ (=10 mg. $CaCO_3$) alone... | 11 c.c. sodium oleate required |
| $CaCl_2$ + 0·2 gram Ca oleate ...... | 11·5—12 c.c. sodium oleate required |

At 60° the results were more like those obtained with magnesium salts at 15°, thus:

| | |
|---|---|
| $CaCl_2$ (=10 mg. $CaCO_3$) ......... | 12·0 c.c. sodium oleate required |
| $CaCl_2$ + 0·1 gram calcium oleate | 15·5 c.c. ,, ,, ,, |
| $CaCl_2$ + 0·2 ,, ,, ,, | 16·0—16·5 c.c. sodium oleate required |

### *Conclusions.*

It is impossible to obtain accurate measurements of hardness in water containing magnesium salts with a soap solution prepared with sodium oleate standardised with calcium salts.

This seems to be due to the fact that magnesium oleate is less soluble than calcium oleate at 15°, and particles of magnesium oleate separate and carry down or adsorb some sodium oleate. With mixtures of calcium and magnesium salts sodium oleate is unsatisfactory, accurate determination being impossible. Heating to higher temperatures up to 60° is of no advantage.

Soaps prepared with the saturated fatty acids are more satisfactory. Potassium myristate makes a stable soap solution, and gives accurate results with calcium and magnesium salts occurring alone or together.

Potassium palmitate solution deposits an acid soap, and is therefore unsuitable for use in the concentration necessary for these titrations.

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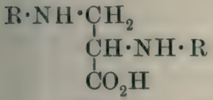
# CV.—*Carbamido- and Other Derivatives of αβ-Dipropylamino- and αβ-Diallylamino-propionic Acids.*

By Edward Percy Frankland and Henry Edgar Smith.

In the present paper the authors show that propylamine and allylamine react with *αβ*-dibromopropionic acid to form dialkylamino-acids (I) analogous in structure to the dimethylaminopropionic acid obtained by Tafel and E. P. Frankland (*Ber.*, 1909, **42**, 3138) from deoxycaffeine, and yielding nitroso- and carbamido-derivatives analogous to those obtained by E. P. Frankland (T., 1910, **97**, 1686) from dibenzylaminopropionic acid; thus, from dipropylamino-propionic acid it was found possible to synthesise a substance having the composition of 1:7-dipropyltetrahydrouric acid (V).

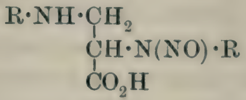
The two alkylamino-acids are strong bases, uniting with an equivalent of hydrobromic acid when prepared by the action of the amine on dibromopropionic acid in alcoholic solution. An attempt to isolate the free dipropylamino-acid gave rise to a substance which, in its non-crystalline character, resembled the corresponding dimethylamino-acid and diaminopropionic acid itself. Both the new acids yield crystalline salts with hydrobromic and with nitric acids, nitroso-derivatives, presumably of the type indicated in formula (II), carbamido-derivatives (III) by the addition of cyanic acid [reasons for the *α*-derivative being formed have been suggested in a previous paper (E. P. Frankland, *loc. cit.*)], hydantoin hydrochlorides (IV) by dehydration with 25 per cent.

hydrochloric acid, and, in the case of the propylamino-compounds, by the further addition of cyanic acid, a substituted tetrahydrouric acid (V):



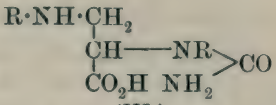
$$\begin{array}{l}\mathrm{R{\cdot}NH{\cdot}CH_2}\\ \quad\quad\mathrm{CH{\cdot}NH{\cdot}R}\\ \quad\quad\mathrm{CO_2H}\end{array}$$

(I.)



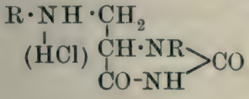
$$\begin{array}{l}\mathrm{R{\cdot}NH{\cdot}CH_2}\\ \quad\quad\mathrm{CH{\cdot}N(NO){\cdot}R}\\ \quad\quad\mathrm{CO_2H}\end{array}$$

(II.)



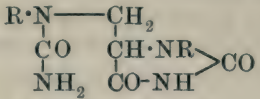
$$\begin{array}{l}\mathrm{R{\cdot}NH{\cdot}CH_2}\\ \quad\quad\left.\begin{array}{l}\mathrm{CH{-\!-}NR}\\ \mathrm{CO_2H\ \ NH_2}\end{array}\right>\mathrm{CO}\end{array}$$

(III.)



$$\begin{array}{l}\mathrm{R{\cdot}NH{\cdot}CH_2}\\ \mathrm{(HCl)}\ \left.\begin{array}{l}\mathrm{CH{\cdot}NR}\\ \mathrm{CO{-}NH}\end{array}\right>\mathrm{CO}\end{array}$$

(IV.)



$$\begin{array}{ll}\mathrm{R{\cdot}N{-\!-\!-}} & \mathrm{CH_2}\\ \mathrm{\ \ \ CO} & \left.\begin{array}{l}\mathrm{CH{\cdot}NR}\\ \mathrm{CO{-}NH}\end{array}\right>\mathrm{CO}\\ \mathrm{\ \ \ NH_2} & \end{array}$$

(V.)

## EXPERIMENTAL.

### A. *Propylamino-derivatives: αβ-Dipropylaminopropionic Acid Hydrobromide.*

Fifty grams of dibromopropionic acid dissolved in 350 c.c. of absolute ethyl alcohol were treated with 63·5 grams of propylamine (5 molecules), and the mixture heated to boiling under reflux for one and a-half hours. The solution, which became warm on adding the amine, and developed a yellow colour, darkened considerably on heating. The alcohol and the excess of propylamine were then removed by distillation, and the residue was treated with an excess of aqueous baryta in order to decompose the propylamine hydrobromide formed during the reaction. The liberated propylamine was distilled off under diminished pressure, the solution freed from barium by the addition of the requisite amount of sulphuric acid, and the barium sulphate removed. The filtrate, which contained neither barium nor sulphuric acid, was evaporated to a small bulk on the steam-bath, and finally concentrated to a brown, pasty mass in a vacuum desiccator. On treatment with a small quantity of pyridine, the dipropylaminopropionic acid hydrobromide could be separated as a white solid, the impurities being removed by the pyridine. The substance was crystallised from aqueous ethyl alcohol, from which it was deposited in minute needles melting and decomposing at 200°.* It was very readily soluble in cold water, the solution being neutral to litmus, sparingly soluble in hot alcohol, and insoluble in ether. The yield of this substance was 60 per cent. of that required by theory:

0·1205 gave 90·36 c.c. $CO_2$ and 9·86 c.c. $N_2$.† C = 40·37; N = 10·28.
0·1090 „ 0·0762 AgBr. Br = 29·75.

$C_9H_{20}O_2N_2$,HBr requires C = 40·15; N = 10·41; Br = 29·74 per cent.

---

* All temperatures here given are uncorrected.

† Carbon and nitrogen combustion in a vacuum. Dry $CO_2$ and $N_2$ at N.T.P.

Smaller yields of the same substance were obtained from solutions of dibromopropionic acid in benzene and in chloroform.

### *Dipropylaminopropionic Acid Nitrate.*

A small quantity of dipropylaminopropionic acid hydrobromide was dissolved in water and treated with a solution of silver nitrate (slight excess over 1 molecule). The mixture was heated on the steam-bath for about an hour, the silver bromide separated, and the slight excess of silver in solution precipitated with hydrogen sulphide. The solution, which had thus been freed from silver, was concentrated and stirred with alcohol, whereupon the nitrate of dipropylaminopropionic acid separated in minute needles, melting and decomposing at 170°. The properties of this substance agreed with those of the hydrobromide:

0·0508 gave 6·77 c.c. $N_2$. N=16·76.

$C_9H_{20}O_2N_2,HNO_3$ requires N=16·73 per cent.

### *Mononitrosodipropylaminopropionic Acid.*

Fifteen grams of dipropylaminopropionic acid hydrobromide were dissolved in a small quantity of water, and treated with silver nitrite (slight excess over one molecule), the mixture being kept cool with ice for about three hours. The silver bromide was then separated, and the excess of silver in solution precipitated by the addition of a drop of dilute hydrochloric acid. The solution, which had been freed from silver, was concentrated in a vacuum desiccator, whereupon the nitroso-compound was deposited in stellate groups of thin prisms. The substance darkened above 200°, and melted with vigorous decomposition at 227°; it was only sparingly soluble in hot water or hot alcohol, and insoluble in ether, the aqueous solution being neutral to litmus. The yield was theoretical. The presence of a nitroso-group was confirmed by the Liebermann test:

0·1101 gave 101·6 c.c. $CO_2$ and 17·1 c.c. $N_2$. C=49·68; N=19·52.

$C_9H_{19}O_3N_3$ requires C=49·77; N=19·36 per cent.

### *β-Propylamino-α-propylcarbamidopropionic Acid.*

A concentrated aqueous solution of 10 grams of dipropylaminopropionic acid hydrobromide was treated with potassium cyanate (slight excess over two molecules), followed by dilute hydrochloric acid (one molecule), and the mixture allowed to remain overnight. On evaporating to a small bulk in a vacuum desiccator, long, needle-shaped crystals were deposited. These were collected, washed with alcohol and with ether, and dried. The product was separated by treatment with hot alcohol into a sparingly soluble fraction, melting and decomposing at 216—217°, and a more readily soluble fraction melting and decomposing at 210°. Both fractions crystallised in prisms. The results of analyses showed the more soluble substance to be the monocarbamido-derivative. It was readily soluble in water, only sparingly so in hot alcohol, and insoluble in ether:

0·1663 gave 0·3141 $CO_2$ and 0·1314 $H_2O$. $C=51·51$; $H=8·78$.
0·1009 „ 96·66 c.c. $CO_2$ and 14·66 c.c. $N_2$. $C=51·58$; $N=18·25$.
$C_{10}H_{21}O_3N_3$ requires $C=51·95$; $H=9·09$; $N=18·18$ per cent.

The less soluble substance, which crystallised out first from the mother liquor, gave the following figures on analysis:

0·1004 gave 83·89 c.c. $CO_2$ and 18·87 c.c. $N_2$. $C=44·98$; $N=23·61$.
0·1014 „ 84·49 c.c. $CO_2$ „ 19·03 c.c. $N_2$. $C=44·86$; $N=23·58$.

The average ratio of nitrogen to carbon is thus 1:2·22, instead of 1:3·33, as required by the substance having the formula $C_{10}H_{21}O_3N_3$.

### γ-*Propylaminomethyl-β-propylhydantoin Hydrochloride.*

2·4 Grams of the crude carbamido-derivative described above were dissolved in a small quantity of 25 per cent. hydrochloric acid, and heated on the steam-bath until a white, crystalline product was deposited. This was collected and recrystallised from aqueous alcohol. The substance forms long prisms (from alcohol), melting and decomposing at 247°; very readily soluble in water, with a strongly acid reaction to litmus, sparingly soluble in alcohol, and insoluble in ether. Yield, 88·5 per cent. of that required by theory:

0·0876 gave 78·22 c.c. $CO_2$ and 11·86 c.c. $N_2$. $C=48·07$; $N=17·00$.
0·2247 „ 0·1290 AgCl. $Cl=14·20$.
$C_{10}H_{19}O_2N_3,HCl$ requires $C=48·29$; $N=16·90$; $Cl=14·29$ per cent.

### 1:7-*Dipropyltetrahydrouric Acid.*

A small quantity of the hydantoin hydrochloride was dissolved in water and treated with a concentrated aqueous solution of potassium cyanate (slight excess over 1 molecule). After remaining at room temperature for three hours the mixture was evaporated to dryness on the steam-bath, and the oily residue extracted with hot alcohol. The tetrahydrouric acid crystallised from the alcoholic solution in minute needles, a theoretical yield being obtained. After recrystallisation from alcohol it melted and decomposed at 184·5°. It was soluble in water or hot alcohol, and insoluble in ether; the aqueous solution being neutral to litmus:

0·0922 gave 87·65 c.c. $CO_2$ and 16·08 c.c. $N_2$. $C=51·18$; $N=21·91$.
$C_{11}H_{20}O_3N_4$ requires $C=51·56$; $N=21·88$ per cent.

### B. *Allylamino-derivatives: αβ-Diallylaminopropionic Acid Hydrobromide.*

This substance was prepared in the same manner as the corresponding propylamino-compound; 50 grams of dibromopropionic acid in 350 c.c. absolute ethyl alcohol with allylamine in the proportion of four and a-half molecules to one of the acid, giving a 51 per cent. yield of the required amino-acid hydrobromide.

The substance crystallised from aqueous alcohol in minute needles melting and decomposing at 182°. It was very readily soluble in water, sparingly so in alcohol, and insoluble in ether:

0·1250 gave 94·95 c.c. $CO_2$ and 10·55 c.c. $N_2$. C = 40·89; N = 10·60.
0·1034 „ 0·0733 AgBr. Br = 30·17.
$C_9H_{16}O_2N_2,HBr$ requires C = 40·76; N = 10·57; Br = 30·18 per cent.

### *Diallylaminopropionic Acid Nitrate.*

Prepared as in the case of the corresponding propylamino-compound and having similar properties. Minute needles (from aqueous alcohol), melting and decomposing at 165°:

0·0542 gave 7·33 c.c. $N_2$. N = 16·99.
$C_9H_{16}O_2N_2,HNO_3$ requires N = 17·00 per cent.

### *Mononitrosodiallylaminopropionic Acid.*

This was prepared as in the case of the corresponding propylamino-compound, and had similar properties. It forms colourless, rectangular plates (from water), darkening above 180°, and melting with vigorous decomposition at 204°:

0·0942 gave 88·22 c.c. $CO_2$ and 14·84 c.c. $N_2$. C = 50·42; N = 19·78.
$C_9H_{15}O_3N_3$ requires C = 50·70; N = 19·77 per cent.

### *Action of Bromine on Diallylaminopropionic Acid Hydrobromide.*

A dilute aqueous solution of the hydrobromide was cooled in a freezing mixture and treated drop by drop with bromine (four molecules), the mixture being frequently stirred.

A pasty, orange-coloured substance was deposited, which, after being thoroughly stirred with the mother liquor, was collected, dissolved in alcohol, and reprecipitated with ether as a pale yellow, flocculent compound, darkening and smelling of bromine on keeping in a vacuum desiccator. On heating, it swelled up between 70°

and 80°; at 100° the yellow colour had disappeared, and a colourless glass remained, which decomposed between 130° and 135°. After further purification by means of alcohol and ether and keeping in a vacuum desiccator, the yellow colour disappeared and an amorphous powder remained, insoluble in cold water and in ether, soluble in warm alcohol:

0·1164 gave 0·1630 AgBr. Br = 59·59.
$C_9H_{16}O_2N_2Br_4$ * requires Br = 63·49 per cent.

### *β-Allylamino-α-allylcarbamidopropionic Acid.*

This substance was prepared under the same conditions as those described for the corresponding propylamino-compound. 12·5 Grams of diallylaminopropionic acid hydrobromide yielded 5·0 grams of a white product, separating in aggregates of minute, needle-shaped crystals. It was collected, washed with alcohol and with ether, and, after drying, melted and decomposed at 194°. After four recrystallisations from aqueous alcohol the melting point was raised to 204·5°. The substance was very readily soluble in water, sparingly so in alcohol, and insoluble in ether:

0·0902 gave 87·85 c.c. $CO_2$ and 13·43 c.c. $N_2$. C = 52·43; N = 18·70.
$C_{10}H_{17}O_3N_3$ requires C = 52·86; N = 18·50 per cent.

### *γ-Allylaminomethyl-β-allylhydantoin Hydrochloride.*

1·2 Grams of the substance described above were converted by the action of 25 per cent. hydrochloric acid into the hydantoin compound, as described in the case of the propylamino-derivative. A theoretical yield was obtained. The substance separated from aqueous alcohol in long prisms, melting and decomposing at 217°. It is extremely soluble in water, sparingly so in alcohol, and insoluble in ether. The aqueous solution was strongly acid to litmus:

0·0932 gave 84·86 c.c. $CO_2$ and 12·81 c.c. $N_2$. C = 49·02; N = 17·27.
0·1990 „ 0·1165 AgCl. Cl = 14·49.
$C_{10}H_{15}O_2N_3,HCl$ requires C = 49·08; N = 17·18; Cl = 14·52 per cent.

1·3 Grams of the hydantoin hydrochloride were treated with potassium cyanate (slight excess over 1 molecule) in aqueous solution. On evaporating to dryness and extracting the residue with alcohol, a colourless, oily product was obtained. This was collected and dried in a vacuum desiccator, and, on grinding, appeared as a hygroscopic, amorphous powder. Yield, 1·5 grams. This substance did not appear to be the required allyltetrahydrouric acid, or, at all events, only an impure specimen of it, analysis showing both the nitrogen and the carbon to be several per cent. lower than the proportions required by theory.

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* Tetrabromodipropylaminopropionic acid.

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## CVI.—*The Estimation of Zinc as Zinc Ammonium Phosphate and Zinc Pyrophosphate.*

By THOMAS MATTHEW FINLAY and ALEXANDER CHARLES CUMMING.

THE method of estimating zinc as zinc ammonium phosphate was first recommended by Tamm (*Chem. News*, 1871, **24**, 148), and has since been investigated by Clark (*J. Soc. Chem. Ind.*, 1896, **15**, 866), Gooch and Austin (*Amer. J. Sci.*, 1898, **6**, 223), and notably by Dakin (*Zeitsch. anal. Chem.*, 1901, **39**, 273).

As Dakin's procedure was closely followed in the experiments of which the results are given in table III, and was found to yield very satisfactory results when a pure zinc solution was used, a brief description may be given.

*Dakin's Method.*—The acid zinc solution, contained in a platinum basin, is almost, but not quite, neutralised with ammonia, diluted to 150 c.c., and warmed on the water-bath. To the warm solution ammonium phosphate is added, the weight of the ammonium phosphate being about ten times the probable weight of the zinc. The precipitate, which is amorphous at first, quickly changes to a fine crystalline precipitate of zinc ammonium phosphate, $ZnNH_4PO_4$. This change takes place more quickly in presence of a considerable amount of ammonium salts.

The solution is heated for fifteen minutes on the water-bath, and set aside for some time. The precipitate is filtered through a Gooch crucible, washed with 1 per cent. ammonium phosphate until free from chloride, and then several times with alcohol or cold water. It is dried at 100—105°, and weighed as $ZnNH_4PO_4$, or, after ignition with exclusion of flame gases, as $Zn_2P_2O_7$.

Dakin also states that where large amounts of ammonium salts are present, it is preferable to ignite directly to the pyrophosphate, owing to the difficulty of removing these salts completely by washing.

Low ("Technical Methods of Ore Analysis," 1911, p. 301) recommends the use of microcosmic salt as precipitant, and to the solution after neutralisation with ammonia he adds 1 c.c. of acetic acid. In some experiments in this laboratory his method was followed, and as the results were sometimes accurate and sometimes very unsatisfactory, a systematic investigation of the method appeared desirable, as it was evident that some slight variation in the conditions of precipitation was the source of the large error.

*Effect of Acidity on the Character of the Precipitate.*—The error noted above was found to be due to precipitation in a solution which was too acid. The precipitate obtained from a neutral solution or one which contained only a trace of free acetic acid was homogeneous, consisting of pure zinc ammonium phosphate. The precipitate obtained from a solution to which 1 c.c. of glacial acetic acid had been added after neutralisation was found, by microscopic examination, to be a mixture of three substances. One portion was amorphous, and consisted of zinc hydroxide or a basic phosphate; a second portion had the characteristic crystalline form of zinc ammonium phosphate; the third portion consisted of groups of needle-shaped crystals, which tended to arrange themselves in tufts round a common nucleus. These crystals imparted to the precipitate its characteristic flocculent appearance. It appeared probable that these crystals were sodium zinc phosphate, and experiment confirmed this supposition. An almost homogeneous precipitate of zinc sodium phosphate was prepared by addition of sodium phosphate to a pure zinc sulphate solution. The crystals thus obtained showed the crystalline arrangement described above.

Zinc sodium phosphate is readily hydrolysed; even on washing with cold water it becomes transformed into amorphous zinc hydroxide or a basic phosphate.

When zinc is precipitated from an acid solution, some zinc remains in solution, but the error from this source is small in comparison with the total error.

## EXPERIMENTAL.

In all experiments, the amount of zinc present was known from the weight of pure zinc sulphate taken.

*Precipitation with Microcosmic Salt in Acid Solution.*—Table I shows the large error introduced by precipitation in a too strongly acid solution. In these experiments, the zinc was precipitated with microcosmic salt, the solution neutralised with ammonia, and 1 c.c. of glacial acetic acid added. The precipitate was ignited and weighed. Column IV gives the weight of zinc on the assumption that the residue was pure zinc pyrophosphate.

TABLE I.

| No. | Zn taken. | Wt. of ppt. | Zn found. | Error. |
|---|---|---|---|---|
| 1 | 0·1389 | 0·2676 | 0·1148 | −0·0241 |
| 2 | 0·1599 | 0·2892 | 0·1241 | 0·0358 |
| 3 | 0·2195 | 0·4198 | 0·1801 | 0·0394 |

The large error is due to the false assumption that the residue was zinc pyrophosphate. Since zinc sodium phosphate forms part of the precipitate, one would expect high results. The results in practice are low, since zinc sodium phosphate is largely hydrolysed by the wash-water, the final residue being largely zinc hydroxide, or a basic salt.

*Precipitation with Microcosmic Salt in Slightly Acid Solution.*—To prevent precipitation of the hydroxide, it is necessary to keep the solution on the acid side of neutrality. Table II gives the results obtained by precipitation with microcosmic salt. After addition of the microcosmic salt, the solution was neutralised with ammonia and then made faintly acid with acetic acid. The precipitate was ignited and weighed as pyrophosphate.

TABLE II.

| No. | Zn taken. | $Zn_2P_2O_7$. | Zn found. | Error. |
|---|---|---|---|---|
| 1 | 0·1993 | 0·4658 | 1·1999 | +0·0006 |
| 2 | 0·1909 | 0·4462 | 0·1915 | 0·0006 |
| 3 | 0 2229 | 0·5218 | 0·2239 | 0·0010 |

It is evident that accurate results are obtainable by precipitation with microcosmic salt, but, as there is less liability to error, we regard precipitation with ammonium phosphate as preferable.

*Precipitation with Ammonium Phosphate.*—Table III shows the results obtained by Dakin's method, that is, precipitation with ammonium phosphate in neutral or faintly acid solution. The first half of the table gives the zinc estimated as $ZnNH_4PO_4$, the second half as $Zn_2P_2O_7$. In No. 5 a platinum vessel was used, and the precipitate showed a tendency to adhere to the sides of the vessel, a difficulty which was not experienced with glass vessels unless a large quantity of ammonium salt was present.

TABLE III.

| No. | Zn taken. | $ZnNH_4PO_4$ found. | Zn found. | Error. |
|---|---|---|---|---|
| 1 | 0·1722 | 0·4708 | 0·1726 | +0·0004 |
| 2 | 0·2015 | 0·5516 | 0·2022 | +0·0007 |
| 3 | 0·1839 | 0·5038 | 0·1846 | +0·0007 |
| 4 | 0·2017 | 0·5520 | 0·2023 | +0·0006 |
| 5 | 0·1636 | 0·4452 | 0·1632 | −0 0004 |
| 6 | 0·1588 | 0·4336 | 0·1590 | +0·0002 |
| 7 | 0·1778 | 0·4854 | 0·1779 | +0·0001 |

TABLE III (*continued*).

| No. | Zn taken. | $Zn_2P_2O_7$ found. | Zn found. | Error. |
|---|---|---|---|---|
| 1 | 0·1722 | 0·4037 | 0·1732 | +0·0010 |
| 2 | 0·2015 | 0·4706 | 0·2019 | +0·0004 |
| 3 | 0·1839 | 0·4298 | 0·1844 | +0·0005 |
| 4 | 0·2017 | 0·4716 | 0·2023 | +0·0006 |
| 5 | 0·1636 | 0·3794 | 0·1628 | −0·0008 |
| 6 | 0·1588 | 0·3716 | 0·1595 | +0·0007 |
| 7 | 0·1778 | 0·4156 | 0·1783 | +0·0005 |

These results show that accurate results are obtained with a pure zinc solution if Dakin's procedure is closely followed. Inaccurate results, however, will be obtained (1) if the solution is alkaline, or (2) if the solution contains any free mineral acid or more than a trace of free acetic acid.

As commercial "ammonium phosphate" is not always the same salt, it is preferable to neutralise with ammonia after addition of ammonium phosphate, and then add 1 c.c. of dilute (about 2*N*) acetic acid. With this procedure it is immaterial whether one uses an acid phosphate or the normal phosphate.

*Precipitation with Potassium and Sodium Phosphates.*—The precipitate obtained when potassium or sodium phosphate is added to a zinc salt in neutral solution behaves like zinc ammonium phosphate, being amorphous at first, but crystallising on keeping. The peculiar crystalline appearance of zinc sodium phosphate has already been noticed; the potassium compound is rather finer-grained than zinc ammonium phosphate. Both zinc potassium phosphate and zinc sodium phosphate remain unchanged on further heating after their water of crystallisation has been driven off. Experiments were carried out to see whether these salts would be suitable forms in which to estimate zinc. The results with potassium proved nearly quantitative, those with sodium were very low. The zinc was completely precipitated in both cases, and the error was apparently due to the fact that both salts are hydrolysed by the subsequent washing water, for phosphate could always be detected in the filtrate even after prolonged washing, although no zinc was dissolved. In the case of zinc potassium phosphate, the loss due to hydrolysis was slight, but increased the more thorough the washing. This will be seen from the following table, where Nos. 1 and 2 show the results after washing about six to eight times, Nos. 3 and 4 show the effect of longer washing, and Nos. 5 and 6 the effect of very prolonged washing. The final washings in all cases contained phosphate, but no zinc. Zinc potassium phosphate is therefore not a suitable form in which to estimate zinc.

### TABLE IV.

*Precipitation with Potassium Phosphate in Neutral Solution.*

| No. | Zn taken. | $ZnKPO_4$ found. | Zn found. | Error. |
|---|---|---|---|---|
| 1 | 0·1775 | 0·5392 | 0·1767 | –0·0008 |
| 2 | 0·1689 | 0·5124 | 0·1680 | 0·0009 |
| 3 | 0·1909 | 0·5774 | 0·1893 | 0·0016 |
| 4 | 0·1555 | 0·4694 | 0·1539 | 0·0016 |
| 5 | 0·1790 | 0·5364 | 0·1758 | 0·0032 |
| 6 | 0·1659 | 0·4998 | 0·1639 | 0·0020 |

### *Precipitation with Ammonium Phosphate in Presence of Sodium and Potassium Salts.*

Whilst the sodium and potassium compounds are not suitable forms in which to estimate zinc, the fact of their formation must be taken into account when precipitating in presence of sodium and potassium salts, for, as might be expected, a mixture of zinc ammonium phosphate and zinc potassium phosphate or zinc sodium phosphate is precipitated. Sodium salts do not present much difficulty, as they can be completely removed in a single precipitation, provided the solution is not too acid and a sufficient quantity of ammonium salt is added. Even when large quantities of sodium salts are present, they can be removed in this way. For example, 5·0 grams of sodium chloride were added to a zinc solution. The zinc was precipitated by ammonium phosphate after addition of 10 grams of ammonium chloride. The precipitate was ignited and weighed as pyrophosphate. Zn taken = 0·1965; Zn found = 0·1963.

Potassium salts are not removed so easily. A single precipitation, even in presence of a large quantity of ammonium salts, is insufficient to prevent partial precipitation of the potassium salt; a double precipitation is necessary, and a large amount of ammonium chloride must be added before each precipitation. A reference to table VI will show that, for complete removal of potassium, it was necessary to add 10 grams of ammonium chloride before each precipitation.

When such large quantities of ammonium salts were present, the precipitate was found to adhere strongly to the sides of the glass beakers used, and could not be completely removed by rubbing. In such cases the traces were dissolved in a little hydrochloric acid and reprecipitated. Dakin has pointed out that when zinc ammonium phosphate is precipitated in presence of large amounts of ammonium salts, it is impossible to remove all the ammonium salts by washing; in all such cases, the precipitate was therefore ignited and weighed as pyrophosphate.

Table V gives the results of estimations in presence of potassium salts. Nos. 1, 2, and 3 were precipitated once. With Nos. 4 and 5 the given amount of ammonium chloride was added before precipitation with ammonium phosphate. The precipitate was collected, washed two or three times, and redissolved in a small quantity of hydrochloric acid. This solution was then neutralised, and the zinc precipitated as before, but without addition of ammonium chloride.

TABLE V.

| No. | Zn taken. | KCl added. | $NH_4Cl$ added. | Zn found. | Error. |
|---|---|---|---|---|---|
| 1 | 0·1726 | 1·0 | none | 0·1904 | +0·0178 |
| 2 | 0·1844 | 2·0 | ,, | 0·2036 | 0·0310 |
| 3 | 0·1772 | 3·0 | 10 grams | 0·1920 | 0·0148 |
| 4 | 0·1576 | 3·0 | 10 ,, | 0·1640 | 0·0064 |
| 5 | 0·1882 | 3·0 | 10 ,, | 0·1950 | 0·0068 |

These results indicate that the amount of potassium in the precipitate may be reduced (1) by a double precipitation, and (2) by adding a large quantity of ammonium chloride before precipitation. Some experiments were therefore tried on the effect of a double precipitation with addition of ammonium chloride before each precipitation. The results are given in table VI. The fourth column gives the amount of ammonium chloride added before both the first and second precipitation.

TABLE VI.

| No. | Zn taken. | KCl added. | $NH_4Cl$. added. | Zn found. | Error. |
|---|---|---|---|---|---|
| 1 | 0·1778 | 0·5 | 5·0 | 0·1775 | −0·0003 |
| 2 | 0·1735 | 1·0 | 5·0 | 0·1745 | +0·0010 |
| 3 | 0·1724 | 1·0 | 10·0 | 0·1722 | −0·0002 |
| 4 | 0·1418 | 1·5 | 10·0 | 0·1415 | −0·0003 |
| 5 | 0·1556 | 2·0 | 10·0 | 0·1559 | +0·0003 |
| 6 | 0·1475 | 3·0 | 10·0 | 0·1472 | −0·0003 |

Accurate results are therefore obtainable in presence of potassium by means of a double precipitation with addition of 5 to 10 grams of ammonium chloride before each precipitation

*Composition of Precipitated Zinc Ammonium Phosphate and Zinc Potassium Phosphate.*—According to Tamm and Dakin, the composition of the precipitated ammonium salt is anhydrous $ZnNH_4PO_4$, but Low gives it as $ZnNH_4PO_4,H_2O$. Experiments on the salt, dried in the air for an hour on a porous plate, showed that constant weight was obtained at 110°, the salt having lost only 0·15 per cent. of its weight; it is therefore anhydrous zinc ammonium phosphate, since the monohydrate would lose 9·2 per cent. by weight on drying. At 150° the salt begins to decompose, leaving the pyrophosphate. Ammonia is freely evolved as the temperature reaches 200°. A sample of precipitated zinc potassium phosphate was dried in the air and weighed. On heating, it became anhydrous at 105°, the loss of weight corresponding with four molecules of water. Precipitated zinc potassium phosphate is therefore probably $ZnKPO_4,4H_2O$, but owing to the difficulty of preparing it in a state of purity this result cannot be considered conclusive.

### *Summary.*

The phosphate method for the estimation of zinc has been investigated to find the reason for occasional unsatisfactory results. It was found that salts of the composition $ZnNaPO_4$ and $ZnKPO_4$ are formed if the solution contains sodium or potassium salts. Precipitation with microcosmic salt yields inaccurate results unless special care is taken to neutralise the solution or to render it very slightly acid with acetic acid after precipitation. In the presence of sodium salts, correct results are obtained by precipitation with ammonium phosphate in neutral solution, after addition of 5 to 10 grams of ammonium chloride. If potassium is present, ammonium chloride must be added before precipitation of the zinc with ammonium phosphate, the precipitate re-dissolved, more ammonium chloride added, and the zinc reprecipitated as before. The precipitate must be ignited and weighed as pyrophosphate.

If due attention is paid to these points, one obtains a crystalline precipitate which is easily manipulated. For a pure zinc solution no more satisfactory method could be desired; in presence of sodium or potassium (more particularly the latter), the method is less satisfactory, but yields accurate results.

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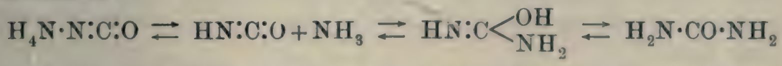
## CVII.—*Mechanism of the Transformation of Ammonium Cyanate into Carbamide, and of the Decomposition of Carbamide by Heat. The Polymerisation of Cyanic Acid.*

By EMIL ALPHONSE WERNER.

THE interesting researches of Walker and his co-workers (T., 1895, **67**, 746; 1897, **71**, 489) have supplied us with most of our present knowledge regarding the phenomena which accompany the transformation of ammonium cyanate into carbamide, both in the dry state and in aqueous or alcoholic solution.

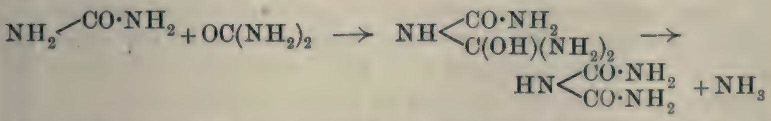
The following are perhaps the most important established facts which support the views and experimental results that form the subject of the present communication: (1) The bimolecular order of the change. (2) The reversibility of the transformation. (3) The partial hydrolysis of ammonium cyanate with production of ammonium carbonate which accompanies the transformation; and (4) The greatly increased velocity of the change of ammonium cyanate into carbamide in an alcoholic, as compared with an aqueous, solution.

Quite recently Chattaway (T., 1912, **101**, 170) has put forward a theory by the aid of which he proposes to explain, not only the probable changes which occur during the transformation of ammonium cyanate into carbamide, but also to account for the formation of biuret and cyanuric acid by the further action of heat on the amide. These changes, together with several related reactions in which cyanic acid and its esters are concerned, he considers may all be simply explained by the well known tendency of the carbonyl group to add on other groups, such as $\begin{smallmatrix}R\\R\end{smallmatrix}\!>\!NH$ or $R\cdot OH$, followed by a subsequent rearrangement involving the migration of a hydrogen atom from oxygen to nitrogen; thus the primary change of ammonium cyanate into carbamide is formulated as follows:



$$H_4N\cdot N{:}C{:}O \rightleftarrows HN{:}C{:}O + NH_3 \rightleftarrows HN{:}C\!<\!\begin{matrix}OH\\NH_2\end{matrix} \rightleftarrows H_2N\cdot CO\cdot NH_2$$

whilst the production of biuret is explained in accordance with the equation:



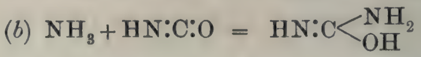
$$NH_2\diagup CO\cdot NH_2 + OC(NH_2)_2 \longrightarrow NH\!<\!\begin{matrix}CO\cdot NH_2\\C(OH)(NH_2)_2\end{matrix} \longrightarrow HN\!<\!\begin{matrix}CO\cdot NH_2\\CO\cdot NH_2\end{matrix} + NH_3$$

the amino-group of one molecule of carbamide reacting with the carbonyl group of another, the hypothetical intermediate product giving rise to biuret by loss of ammonia, and by a repetition of these changes, cyanuric acid is ultimately formed, no less than three hypothetical intermediate products being supposed to take part in the changes before the atomic complex, $HN\!<\!\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\!>\!CO$, is produced. Whilst this can scarcely be considered a simple explanation of the phenomena in question, this theory, as is pointed out in the following, is open to several serious objections, besides which it fails to explain some of the established facts connected with the different changes, and in the present author's opinion does not possess the required agreement with experimental evidence to secure its general acceptance as a likely explanation of the well known reactions under consideration.

Commencing with the primary change, the first point subject to criticism is the constitution of ammonium cyanate itself. Chattaway considers this salt to be derived from the *iso*-, or, more correctly, the keto-form of the acid; and as dissociation proceeds with application of heat, the dissociated products re-unite to form carbamide, no change in the constitution of the cyanic acid being assumed to occur. Bearing in mind that the many reactions, attributed to the tendency of the carbonyl group to add on such groups as cited by Chattaway, take place readily at the ordinary temperature, it is difficult to understand why ammonium cyanate should be produced at all if cyanic acid is considered to be $\mathrm{H{\cdot}N{:}C{:}O}$ only; for instance, there seems no reason why the two reactions:

$$(a)\ \mathrm{NH_3+HN{:}C{:}O\ =\ NH_4{\cdot}N{:}C{:}O}$$

and



$$(b)\ \mathrm{NH_3+HN{:}C{:}O\ =\ HN{:}C{<}^{NH_2}_{OH}}$$

should take place at the same temperature (see Expts. 1, 2, 3, and 4), unless it be assumed that cyanic acid at low temperatures is predisposed to react in accordance with equation (*a*), since at 0°, for example, the product of the interaction is ammonium cyanate only. That a condition of equilibrium between the reaction products should be capable of arising from such a cause is very improbable.

If a change in the configurations of the cyanic acid molecule from $\mathrm{HO{\cdot}C{\vdots}N}$ to $\mathrm{HN{:}C{:}O}$ with rise of temperature be admitted, all the phenomena connected with the transformation of ammonium cyanate into carbamide and of the decomposition of the latter by heat can be easily explained in a very simple manner, which is, moreover, shown in the following to be in complete accord with all the known facts.

It is only necessary to refer in general to the extensive work of E. Fisher on uric acid and its derivatives, and in particular to the interesting results of Hantzsch and Bauer (*Ber.*, 1905, **38**, 1005) and Hantzsch (*Ber.*, 1906, **39**, 139) on the constitution of the metallic salts of cyanuric acid and on the production of mixed *N*-alkyl and *O*-alkyl derivatives, to show that the formation of derivatives containing the complex $\mathrm{R{\cdot}O{\cdot}C{:}N{\cdot}}$ from compounds containing the group $\mathrm{{\cdot}NH{\cdot}CO{\cdot}}$ is determined by the electropositive character of the element or radicle taking part in the change.

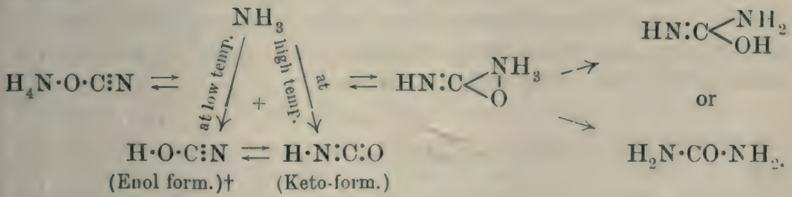
It seems only natural to suppose that the group $\mathrm{HN{:}CO}$, in the free state, should behave in a similar manner, under the same influence. The experimental results, in fact, appear to favour the view that cyanic acid is capable of existing in equilibrium in the two forms, the relative proportions being a function of the temperature.

The two best known properties of ammonium cyanate, namely, its hydrolysis to ammonium carbonate, noticed by Walker (*loc. cit.*), and its transformation into carbamide are strong evidence in support of the constitutional formula $H_4N{\cdot}O{\cdot}CN$; thus, cyanic acid in its enolic form may be considered as "carbonicnitril," and the hydrolysis of the ammonium salt expressed as follows:

$$H_4N{\cdot}O{\cdot}C{\vdots}N + H_2O \longrightarrow H_4N{\cdot}O{\cdot}CO{\cdot}NH_2 + H_2O \longrightarrow H_4N{\cdot}O{\cdot}CO{\cdot}ONH_4,$$

ammonium carbamate being, no doubt, an intermediate product. Assuming the formula $H_4N{\cdot}N{:}C{:}O$,* the change by hydrolysis is by no means simple to follow, even admitting the presence of the ions $H_4N$ and NCO in solution.

Being a weak acid in the enolic form (comparable to HOCl), cyanic acid would naturally yield a very unstable ammonium salt, easily dissociated by heat, both in the dry state and in solution, and transformable into carbamide according to the following scheme:



The formula $HN{:}C{<}^{NH_3}_{O}$, which is used in the above to show the production of carbamide from the union of ammonia with $H{\cdot}N{:}C{:}O$, is an extension of the formula recently proposed by the author to represent the constitution of thiocarbamide in the static condition (T., 1912, **101**, 2185): no particular stress is laid on its acceptance in the above scheme until experimental evidence is forthcoming to support it, and whilst it helps to throw some light on the ultimate appearance of carbamide in either the symmetrical or unsymmetrical form, it is obvious that its removal from the scheme will not affect the meaning which this is intended to convey. Whilst carbamide is much more stable than ammonium cyanate, when it is heated above its melting point it also undergoes dissociation into ammonia and cyanic acid (chiefly in the keto-form), and gives a sublimate which, under ordinary conditions contains from 28 to 30 per cent. of ammonium cyanate, whilst if the vapours are artificially cooled, this may be increased to over 40 per cent. (see Experimental part); the rest of the sublimate is carbamide; if the vapour is kept warm, the sublimate, as might be expected, consists entirely of carbamide.

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* This constitution is based solely on analogy to KCNO; reactions of the type $KCNO + RX = R{\cdot}NCO + KX$ are no proof that the potassium salt must be KNCO; the constitution depends entirely on the electro-chemical nature of the element or radicle entering into the change; the properties of potassium cyanate are more in agreement with the constitution KOCN than KNCO.

† Since the group $\cdot HN{\cdot}CO\cdot$ shows great analogy in its behaviour to the group $\cdot CH_2{\cdot}CO\cdot$, the distinctive terms "enol" and "keto" are equally well applicable to the former group, and are used here in preference to the usual unsuitable terms "normal" and "*iso*" for the two forms of cyanic acid.

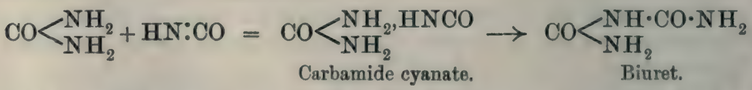
These results show that the dissociation product must contain cyanic acid both in the enol and keto-forms, the proportions varying with the temperature; the enol form, which is alone responsible for the presence of ammonium cyanate in the sublimate, is not capable of existing at the higher temperature.

The reversion of carbamide to ammonium cyanate first pointed out by Walker and Hambly (*loc. cit.*) is easily explained by the views embodied in the above scheme; it is evident that carbamide undergoes a certain amount of dissociation in aqueous solution, even at the ordinary temperature; under such conditions some of the cyanic acid will assume the enol form, and in presence of ammonia will give rise to the cyanate.

### *Production of Biuret and Cyanuric Acid from Carbamide.*

The dissociation of carbamide by heat has not been considered by Chattaway in his explanation of the origin of biuret and cyanuric acid respectively by the decomposition of the amide, stress being laid solely on the evolution of ammonia, and both products are supposed to be formed by the mutual interaction of carbamide molecules in the manner already referred to.

All the experimental evidence, however, is in favour of the view that the cyanic acid set free by dissociation is responsible for the production of the biuret and cyanuric acid, the former resulting from its reaction with unchanged carbamide in the following manner:



$$CO\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + HN\!:\!CO = CO\begin{matrix}\diagup NH_2,HNCO\\ \diagdown NH_2\end{matrix} \longrightarrow CO\begin{matrix}\diagup NH\cdot CO\cdot NH_2\\ \diagdown NH_2\end{matrix}$$

Carbamide cyanate. Biuret.

As is well known, when carbamide is heated alone the yield of biuret is very poor; the conditions are unfavourable for the realisation of the above reaction, much of the cyanic acid undergoes polymerisation to cyanuric acid at the high temperature, whilst another portion is volatilised along with ammonia.

Schiff's improved method for preparing biuret (*Ber.*, 1896, **29**, 298) by heating carbamide hydrochloride to a temperature not exceeding 130°, whereby a yield amounting to 45—50 per cent. of the carbamide taken may be easily obtained, is readily explained; the disturbing influence of the ammonia is removed by its conversion into ammonium chloride, whilst the low temperature retards the polymerisation of the cyanic acid.

The above reaction has, in fact, been realised long ago by Finckh (*Annalen*, 1861, **124**, 336), who showed that biuret may be prepared by passing the vapour of cyanic acid directly into carbamide heated to its melting point; moreover, in recent years several substituted biurets and thiobiurets have been prepared by analogous reactions.

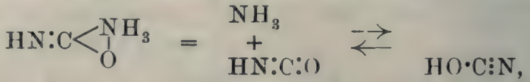
When biuret is heated above its melting point (190°) it decomposes rapidly, giving off ammonia and cyanic acid; by artificially cooling the vapour a quantity of sublimate may be easily obtained; this was found in a single experiment to contain as much as 42—43 per cent. of ammonium cyanate, together with carbamide; the residue after heating was mainly cyanuric acid.

It is evident, therefore, that cyanic acid, as well as ammonia, is produced throughout the whole course of the changes, and since cyanuric acid, as pointed out by Hantzsch (*Ber.*, 1905, **38**, 1013), is a product of the polymerisation of cyanic acid at high temperatures, in contrast to cyamelide which is a product of an analogous change at low temperatures, it seems quite unnecessary to look outside this cause for the origin of cyanuric acid as a product of the decomposition of carbamide. It also explains why the polymeride appears at the very outset of the decomposition of carbamide, simultaneously with the biuret, and if any cyanuric acid is produced other than by polymerisation of $HN\colon C\colon O$, it seems more likely to result from an interaction between biuret and cyanic acid on the same lines as in the last equation, rather than between biuret and unchanged carbamide, as suggested by Chattaway in his theory.

### *Constitution of Carbamide in the Static Condition.*

It is rather remarkable that the dissociation of carbamide by heat, with formation of cyanic acid as a volatile product, has not received proper consideration; the general impression appears to be that carbon dioxide is one of the products which accompanies ammonia during the decomposition of carbamide by heat; even in such a recent work as "Organic Chemistry of Nitrogen" (Sidgwick, 1910, p. 186) the following statement occurs: "When urea is strongly heated it breaks up with the formation of ammonia, carbon dioxide, biuret, and cyanuric acid," the latter being correctly attributed to the rapid polymerisation of cyanic acid as fast as it is set free. It is obvious that the formation of carbon dioxide would involve a secondary decomposition either between two molecules of carbamide, or one in which water is formed, which would then hydrolyse the cyanic acid with production of carbon dioxide.

When the structural formula for carbamide suggested by the writer is considered, there appears no reason why the decomposition by heat should not be a simple and straightforward change, thus:



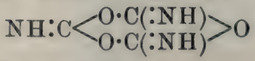
$$\mathrm{HN{:}C}<^{\mathrm{NH_3}}_{\mathrm{O}} \quad = \quad \begin{matrix}\mathrm{NH_3}\\ + \\ \mathrm{HN{:}C{:}O}\end{matrix} \quad \rightleftarrows \quad \mathrm{HO{\cdot}C}\vdots\mathrm{N},$$

in which no secondary products are formed, so far as the volatile substances are concerned. This view has been confirmed by direct experiment, the results of which prove conclusively that carbon dioxide is not a product of the decomposition by heat of pure dry carbamide. The change is a simple case of dissociation, and, as indicated by the above equation, ammonia and cyanic acid are the sole volatile products, the presence of the latter being, no doubt, responsible for the erroneous idea that carbon dioxide is one of the decomposition products.

Experimental evidence in support of the constitution of carbamide here proposed is deferred to a future communication.

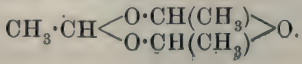
### *The Formation of Cyamelide and Cyanuric Acid from Cyanic Acid.*

The polymerisation of cyanic acid at low temperatures, with production of cyamelide, has an important bearing on the views put forward by the writer regarding the relations of the two forms of cyanic acid. Van't Hoff ("Chemical Dynamics," p. 110) has shown that the change of cyanic acid to cyamelide is no doubt a termolecular reaction; Hantzsch (*Ber.*, 1905, **38**, 1016), from a study of its chemical properties, has proposed a constitutional formula for cyamelide which is in all probability a correct representation of the structure of the compound. It is concluded that cyamelide cannot contain either the group HO·CN or the group HN·C·O, and is hence very likely a polymeride resulting from the union of three molecules of cyanic acid through the intervention of oxygen, thus:



$$\mathrm{NH{:}C}<^{\mathrm{O{\cdot}C({:}NH)}}_{\mathrm{O{\cdot}C({:}NH)}}>\mathrm{O}$$

and comparable to paracetaldehyde:



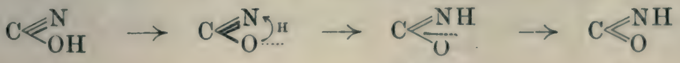
$$\mathrm{CH_3{\cdot}CH}<^{\mathrm{O{\cdot}CH(CH_3)}}_{\mathrm{O{\cdot}CH(CH_3)}}>\mathrm{O}.$$

Hantzsch's conclusion that cyamelide must be considered as a condensation product derived from ψ-cyanic acid, that is, the keto-form, $HN:C:O$, does not necessarily follow from the above formula, and is open to criticism, since it still leaves unanswered the question: "Why is cyamelide formed along with cyanuric acid under the conditions stated."

When cyanic acid undergoes polymerisation, the change, as well known, is very rapid, and is accompanied by much development of heat, and the product is a mixture of the two polymerides; in the particular experiment recorded by Senier and Walsh (T., 1902, **81**, 290), as much as 70 per cent. of the product was found to be cyanuric acid. Hantzsch's experiments (*loc. cit.*) have shown that the conditions favourable to the formation of cyamelide are slow polymerisation and a low temperature; and Walker's observation of the production of some cyamelide during the slow transformation of ammonium cyanate into carbamide at 61° is of particular interest in this connexion.

The mechanism of the formation of cyamelide and cyanuric acid becomes intelligible if the tendency of the two forms of cyanic acid to co-exist in equilibrium be taken into consideration, and may be explained as follows. Cyanic acid represents an unstable group of atoms, which is incapable of assuming a simple* molecular configuration which can give rise to a condition of static equilibrium, an end which is only attained by polymerisation to a six-membered ring, the most stable form of cyclic molecules.

The enol-form of the acid is apparently the less stable, and tends to change to the more stable keto-form, thus:



Enol. Phase (*a*). Phase (*b*). Keto.

Since an interval of time must elapse, while the hydrogen atom has migrated from oxygen to nitrogen, either a valency of the oxygen atom becomes momentarily free (*a*), followed immediately by a momentary liberation of a carbon valency (*b*) when the hydrogen atom unites with nitrogen, or when the hydrogen atom has attained a position as represented in (*a*) a simultaneous liberation of the respective valencies occurs, their union within the molecule giving rise to the keto-form of the acid. Since this is also an unstable configuration, it is natural to conclude that the chief result will be the formation of cyamelide by the union of three molecules when in the state represented by phase (*b*), the free valency of the oxygen atom of one molecule uniting with the free valency of the carbon atom of another, thus:

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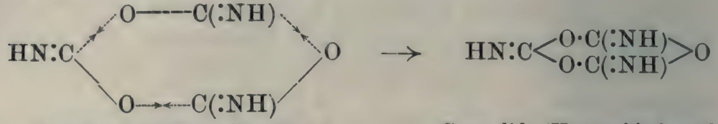
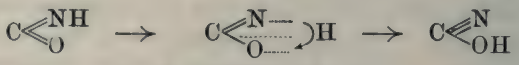
* Neither fulminic acid, $C:NOH$, nor formonitrile oxide, $\underset{\diagdown O \diagup}{CH:N}$, has been isolated.



Three molecules in phase (*b*). Cyamelide (Hantzsch's formula).

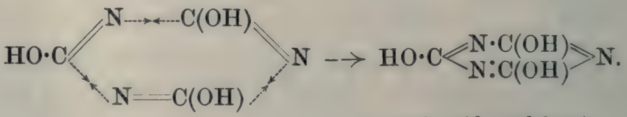
According to this theory, cyamelide is not the result of the polymerisation of cyanic acid pre-existing in the keto-form ($\psi$-acid of Hantzsch), but is the product of the natural tendency to stable equilibrium formed while the acid is in the act of changing from one form to the other. It also explains a third condition which is necessary in order that cyamelide may be formed, namely, that the cyanic acid must be primarily in the enol form.

When cyanic acid is generated at a high temperature, as during the dissociation of carbamide by heat, it is liberated solely in the keto-form, which polymerises at once to cyanuric acid, no cyamelide being formed. In this case the polymerisation originates as follows:



Keto. Intermediate phase (*a*). Enol.

the conditions being altogether unfavourable for the existence* of $HO{\cdot}C{\vdots}N$; the latter cannot be formed by union of the momentary free valencies of the carbon and nitrogen atoms within the molecule itself, and hence a state of stable equilibrium is attained by the union of three molecules in phase (*a*) to form cyanuric acid the moment the hydrogen atom has entered into union with oxygen, thus:



Cyanuric acid (enol form).

It is obvious that cyamelide cannot be formed in the above reaction; on the other hand, cyanuric acid is largely formed during the production of cyamelide (Senier and Walsh, *loc. cit.*), a fact which the present theory is capable of predicting, namely, since the keto-form of cyanic acid is produced simultaneously with the cyamelide, in accordance with the first scheme, and also in consequence, simultaneously with the disappearance of the enol acid, it

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* Although $HO{\cdot}CN$ cannot exist free at the temperature, the tendency of $HN{:}CO$ to co-exist in equilibrium with it would still persist, from which cause the polymerisation takes effect.

(the keto-acid) becomes immediately polymerised to cyanuric acid in an endeavour to restore equilibrium by giving rise to more of the enol form, in accordance with the second scheme.

There is little doubt that the thermal effect which accompanies the polymerisation of liquid cyanic acid must have an important influence on the relative proportions of the two polymerides produced in a given experiment, and it is very likely that if cyanic acid were allowed to undergo slow polymerisation at a very low temperature a much larger proportion of cyamelide would be produced than was found by Senier and Walsh in the single case recorded by them.

The production of a small quantity of cyamelide from ammonium cyanate at 61° (Walker, *loc. cit.*) confirms the view that cyanic acid in the form $HO{\cdot}C{\vdots}N$ results from the dissociation of the ammonium salt.

The theories which have been put forward in the present communication to explain the several phenomena discussed can lay claim to be in complete agreement with all the experimental facts, and no series of hypothetical intermediate compounds is introduced to hamper their simplicity. All the different changes can be referred to the two fundamental causes:

(1) Dissociation, and (2) the reversible reaction:

$$HO{\cdot}C{\vdots}N \rightleftharpoons HN{:}CO.$$

In the face of all the evidence, Chattaway's conclusion that "the oldest and best-known instance of isomeric change is not a case of isomeric change at all" is not justifiable; there exists no reason for removing Wöhler's historical discovery from its time-honoured position of being the first example of isomeric change on record.

## EXPERIMENTAL.

Qualitative experiments have shown that when carbamide or biuret are decomposed by heating in a long test-tube the sublimate formed consists of ammonium cyanate and carbamide, the proportions of which vary with the temperature and rate of heating.

Soluble cyanates can be rapidly estimated with a fair degree of accuracy by direct titration with $N/10$-silver nitrate, using neutral chromate as indicator; the estimation is not interfered with by the presence of carbamide in excess.

Example I: 0·098 KOCN (Kahlbaum) dissolved in 20 c.c. of water.

$N/10$-$AgNO_3$ required = 11·2 c.c.; KOCN = 92·5 per cent.

Example II: 0·1935 KOCN (freshly prepared by action of potassium hydroxide on urethane in alcoholic solution; Mulder, *Rec. trav. chim.*, 1888, **6**, 170) dissolved in 40 c.c. of water.

$N/10$-$AgNO_3$ required = 23·4 c.c.; KOCN = 98·07 per cent.

In all the following experiments 4 grams of well-dried powdered carbamide were heated in a dry test-tube 2·5 cm. wide and 18 cm. long, closed with a cork carrying a piece of narrow glass tubing about 15 cm. to exclude moisture from the air during the heating. The tube was held in a nearly horizontal position.

*Expt.* 1.—Carbamide heated at a moderate rate until the liquid just became opalescent. Tube quickly cooled under the water tap, and the greater part of the sublimate removed by means of a steel spatula, and at once analysed.

Sublimate = 0·0241.

$N/10$-$AgNO_3$ required = 1·2 c.c.; $NH_4OCN$ = 29·8 per cent.

*Expt* 2.—Same as above.

Sublimate = 0·09.

$N/10$-$AgNO_3$ = 4·4 c.c.; $NH_4OCN$ = 28·8 per cent.

*Expt.* 3.—Carbamide heated slowly, front of tube, to extent of 8 cm., surrounded by a coil of narrow lead piping carrying a current of cold water.

Sublimate = 0·1215.

$N/10$-$AgNO_3$ = 7·4 c.c.; $NH_4OCN$ = 36·5 per cent.

*Expt.* 4.—Carbamide heated very rapidly, vapour cooled as in Expt. 3.

Sublimate = 0·151.

$N/10$-$AgNO_3$ = 10·4 c.c.; $NH_4OCN$ = 41·3 per cent.

Thus the artificial cooling of the vapour, as was to be expected, increased the proportion of ammonium cyanate in the sublimate. Since the rate of heating might be expected to have an influence on the proportion of cyanic acid that would escape polymerisation, the following two experiments were made. Hantzsch has shown that cyanuric acid may be accurately titrated with sodium hydroxide solution, using phenolphthalein as indicator; it then behaves as a monobasic acid, $H(H_2C_3N_3O_3)$.

*Expt.* 5.—Carbamide heated very slowly, vapour not artificially cooled.

Sublimate = 0·0786.

$N/10$-$AgNO_3$ = 3·8 c.c.; $NH_4OCN$ = 29 per cent.

Residue = 2·44 dissolved in water. $N$-NaOH = 2 c.c. Cyanuric acid = 10·57 per cent.

*Expt.* 6.—Carbamide heated very rapidly, as in Expt. 5.

Sublimate = 0·0955.

$N/10$-$AgNO_3$ = 5·6 c.c.; $NH_4OCN$ = 35·18 per cent.

Residue = 2·34. $N$-NaOH = 2·6 c.c. Cyanuric acid = 14·33 per cent.

Whilst the polymerisation increases with the rate of heating, more cyanic acid is able to escape during the rapid heating, and hence the larger proportion of ammonium cyanate in the sublimate.

*Expt.* 7.—Biuret (2 grams) heated in test-tube until fluid commenced suddenly to thicken. Vapour artificially cooled.

Sublimate = 0·066.

$N/10$-$AgNO_3$ = 4·7 c.c.; $NH_4OCN$ = 42·7 per cent.

*Expt.* 8.—Biuret heated as above. Sublimate examined under microscope had characteristic fern-leaf-like formation (due to $NH_4OCN$); the tube was now immersed to the neck in boiling water for a few minutes; the sublimate changed in appearance, and under the microscope was seen to consist of well-defined, broad-angled prisms. The solution of the crystals in water gave no precipitate with silver nitrate; some of the solution gave, with nitric acid in excess, characteristic crystals of carbamide nitrate. A similar result can be obtained with carbamide; the sublimate in the first instance, if dissolved in water, gives a copious precipitate with silver nitrate; after warming and then dissolving in distilled water a solution is obtained, which gives at most only a faint opalescence with silver nitrate. As both experiments can be performed in a few minutes, they form the subject of an interesting and instructive lecture demonstration to support the theories put forward. Further experiments are in progress over a more extended series of conditions.

### *Examination of the Gaseous Products Evolved during the Decomposition of Carbamide by Heat.*

*Expt.* 9.—Five grams of finely powdered and well-dried carbamide were heated in a dry test-tube (2·5 cm. by 18 cm.), provided with a delivery tube dipping to the bottom of 50 c.c. of absolute alcohol contained in a flask immersed in ice-cold water. The carbamide was heated rapidly until the liquid became suddenly opalescent, indicating separation of cyanuric acid, whilst the tube was maintained in an almost horizontal position. A crystalline precipitate formed in the alcoholic solution, whilst the latter contained much free ammonia. The solution was poured off from the crystals, which were rapidly washed with a small quantity of fresh alcohol.

The solution of the crystals in water, and also the alcoholic solution, gave the following reactions:

(1) Addition of calcium chloride solution—no immediate precipitate in the cold; slight opalescence after ten minutes; a copious precipitate of calcium carbonate on warming.

(2) A portion of each solution was heated in a test-tube immersed in boiling water for five minutes, and then cooled; on addition of calcium chloride a faint opalescence was obtained, which was not sensibly increased by warming.

This last result could not be obtained if either ammonium carbamate or carbonate * was present in the crystals or in the alcoholic solution; the absence of a precipitate of calcium carbonate in the second case being due to the disappearance of the ammonium cyanate by its conversion into carbamide on heating.

*Expt.* 10.—Carbamide was heated as before; the gas evolved was collected over mercury after expulsion of all the air; 50 c.c. of gas so obtained was found to be completely dissolved by 2 c.c. of water, and the solution gave no opalescence with calcium chloride.

These results prove that ammonia and cyanic acid are the only volatile products, and no carbon dioxide is present when dry carbamide is heated.

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# CVIII.—*The Synthetical Preparation of the* d-*Glucosides of Sitosterol, Cholesterol, and Some Fatty Alcohols.*

By ARTHUR HENRY SALWAY.

IT has recently been shown (T., 1913, **103**, 399) that phytosterol glucosides are of frequent occurrence in plants. These substances, which have been designated phytosterolins, vary to some extent in composition and character according to the plant from which they have been isolated. In many cases the phytosterolin appears to consist of sitosterol-*d*-glucoside, $C_{27}H_{45}O\cdot C_6H_{11}O_5$, whilst in other instances it seems to be a mixture of this substance with the glucoside of stigmasterol, $C_{30}H_{49}O\cdot C_6H_{11}O_5$. In order to obtain additional information regarding the character of these natural substances, it was deemed of importance to attempt the synthesis of a phytosterol glucoside, and compare its properties with those of the naturally occurring phytosterolins. The phytosterol chosen for this purpose was sitosterol, $C_{27}H_{46}O$, since the latter can be prepared in comparatively large quantities from wheat germ, and is uncontaminated with stigmasterol when obtained from this source. It was converted into the glucoside by treatment with bromoacetoglucose in ethereal solution in the presence of dry silver oxide. The sitosterol-*d*-glucoside thus obtained was found to possess properties closely resembling the phytosterolins, and there is no doubt that the substances previously designated ipuranol, cluytianol, and trifolianol consist almost entirely of sitosterol-*d*-glucoside.

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* This would be formed if water accompanied the carbon dioxide and ammonia.

In addition to the synthesis of sitosterol-*d*-glucoside, the glucosides of cholesterol, myricyl alcohol, ceryl alcohol, and cetyl alcohol have been prepared. These glucosides have not hitherto been found in nature, but it appears probable, in the light of recent observations, that the glucosides of the fatty compounds, ceryl, cetyl, and myricyl alcohols, do occur in small quantities in plants, and that they have not hitherto been isolated owing to the difficulty attending their separation. The synthesis of these glucosides was of importance, since a knowledge of their properties would greatly facilitate the future examination of plants for the presence of such substances.

It was also intended to prepare the glucoside of the so-called *iso*cholesterol, and a commercial specimen of the latter was procured for the purpose. The material was found, however, to be a very impure mixture of substances, since it contained considerable quantities of cholesterol and carnaubyl alcohol, $C_{24}H_{50}O$, and no substance agreeing with the *iso*cholesterol of Schulze and his pupils (*J. pr. chem.*, 1873, [ii], **7**, 163; 1874, [ii], **9**, 325; 1882, [ii], **25**, 159), or of Darmstädter and Lifschütz (*Ber.*, 1898, **31**, 97), could be isolated from it. It may furthermore be noted in this connexion that the statements of the above-mentioned authors concerning the properties and composition of *iso*cholesterol are so conflicting that further investigation of the subject is desirable.

The question whether the glucosides prepared in this investigation belong to the α- or β-series has been left undecided on account of the fact that the insolubility of these substances in water renders the emulsion test for α- and β-glucosides indecisive. Fischer and Helferich (*Annalen*, 1911, **383**, 68) have shown, however, that in almost all cases the method of preparation of glucosides described by them, and adopted in the present investigation, leads to the formation of β-glucosides, so that the glucosides now obtained probably belong also to this series. In the case of ceryl-*d*-glucoside, however, it is of interest to note that the present author has isolated two distinct modifications, which may possibly represent the α- and β-forms of the glucoside, although no definite evidence to this effect has been obtained.

The formation of two modifications of ceryl-*d*-glucoside, $C_{27}H_{55}O\cdot C_6H_{11}O_5$, is of some interest in connexion with an observation of E. Fischer and Helferich (*loc. cit.*) regarding the properties of cetyl-*d*-glucoside, $C_{16}H_{33}O\cdot C_6H_{11}O_5$. These investigators showed that cetyl-*d*-glucoside melts indefinitely, beginning to change at 78° and finally melting at about 145°; it now seems probable, in view of the results obtained with ceryl-*d*-glucoside, that this behaviour is due to the presence of two modifications. In order to ascertain whether this were the case, cetyl-*d*-glucoside was prepared, but although it was found to possess the properties described by Fischer and Helferich, it was not possible to separate the two modifications.

## EXPERIMENTAL.

### I. *Sitosterol*-d-*glucoside*, $C_{27}H_{45}O\cdot C_6H_{11}O_5$.

The sitosterol required for the preparation of this compound was obtained from wheat-germ (compare Burian, *Monatsh.*, 1897, **18**, 551). The fatty oil from 50·8 kilos. of the latter was hydrolysed with an excess of potassium hydroxide in the presence of alcohol, and the resulting soap solution extracted repeatedly with ether. The ethereal solution was then evaporated, and the residue crystallised from ethyl acetate, when the sitosterol was obtained in colourless needles, melting at 138°. The amount of pure substance isolated from 50·8 kilos. of wheat germ was 130 grams (compare Pickard, T., 1908, **93**, 1928). It possessed the specific rotation $[\alpha]_D -32{\cdot}2°$ ($c = 2{\cdot}9$ with chloroform), and on analysis gave results agreeing well with the formula $C_{27}H_{46}O$.

In order to ascertain whether the material was quite free from stigmasterol, it was acetylated, and the acetyl derivative treated with bromine according to Windaus and Hauth's method (*Ber.*, 1906, **39**, 4378), but a negative result was obtained, thus showing the absence of stigmasterol.

For the conversion of sitosterol into its glucoside, 15 grams of anhydrous substance and 15 grams of pure bromoacetoglucose were dissolved in dry ether and shaken continuously for eight hours with freshly precipitated, dry silver oxide. The mixture was then filtered, a little dilute nitric acid having been previously added to coagulate the silver oxide and facilitate the filtration, after which the ethereal filtrate was washed, dried, and evaporated. The residue was next crystallised once from alcohol to remove a small amount of soluble by-product formed from the bromoacetoglucose. The substance thus obtained then consisted of a mixture of tetra-acetylsitosterol-*d*-glucoside and unchanged sitosterol, and could not be resolved into its components by direct fractional crystallisation. It was therefore dissolved in hot alcohol, and the solution digested for about a minute with an excess of potassium hydroxide. In this manner the acetyl groups of the glucoside were eliminated without affecting the remaining part of the molecule, and the free glucoside, which is only sparingly soluble in hot alcohol, was deposited. This was collected, washed with hot alcohol, and purified by crystallisation from a mixture of pyridine and alcohol, when it separated in rosettes of small, colourless needles. When heated in a capillary tube, the substance begins to soften at about 270°, and melts and decomposes at 295—300°. The yield of pure substance amounted to 4 grams:

0·1028 gave 0·2721 $CO_2$ and 0·0960 $H_2O$. C = 72·2; H = 10·4.
$C_{33}H_{56}O_6$ requires C = 72 3; H = 10·2 per cent.

*Sitosterol*-d-*glucoside*, $C_{27}H_{45}O\cdot C_6H_{11}O_5$, is insoluble in water and only sparingly soluble in alcohol, ether, chloroform, or benzene. It dissolves readily in pyridine, and can be easily crystallised from this solvent in admixture with alcohol. It yields the characteristic colour reaction of the phytosterols when dissolved in acetic anhydride and chloroform, and a drop of concentrated sulphuric acid then added. When heated with aqueous hydrochloric acid in the presence of amyl alcohol it is readily resolved into its components, sitosterol and dextrose.

*Tetra-acetylsitosterol*-d-*glucoside*, $C_{27}H_{45}O\cdot C_6H_7O_5Ac_4$.—This substance was prepared by heating the glucoside for thirty minutes with an excess of acetic anhydride. The greater part of the latter was then removed by distillation, alcohol added to the residue, and the crystalline solid which separated then recrystallised from alcohol. It was thus obtained in colourless, glistening leaflets, melting at 166—167°:

0·1010 gave 0·2540 $CO_2$ and 0·0812 $H_2O$. C = 68·6; H = 8·9.
$C_{41}H_{64}O_{10}$ requires C = 68·7; H = 8·9 per cent.
0·5694, made up to 20 c.c. with chloroform, gave $\alpha_D$ $-1°18'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-22·9°$.

Tetra-acetylsitosterol-*d*-glucoside is very readily soluble in ether, chloroform, benzene, or hot alcohol, but only sparingly so in cold alcohol. It is immediately hydrolysed in the presence of alkali hydroxides with regeneration of the glucoside.

*Tetrabenzoylsitosterol*-d-*glucoside*, $C_{27}H_{45}O\cdot C_6H_7O_5Bz_4$.—In order to obtain this compound, sitosterol-*d*-glucoside was dissolved in pyridine, and the solution gently warmed for about a minute with an excess of benzoyl chloride. The mixture was then poured into alcohol, when the benzoyl derivative separated as a flocculent precipitate. This was collected and purified by crystallisation from chloroform and alcohol, when it was obtained in slender, colourless needles, melting at 198°:

0·1075 gave 0·2988 $CO_2$ and 0·0721 $H_2O$. C=75·8; H=7·5.

$C_{61}H_{72}O_{10}$ requires C=75·9; H=7·5 per cent.

0·4733, made up to 20 c.c. with chloroform, gave $\alpha_D$ +0°52′ in a 2-dcm. tube, whence $[\alpha]_D$ +18·3°.

Tetrabenzoylsitosterol-*d*-glucoside is readily soluble in chloroform, ethyl acetate, or benzene, but sparingly so in alcohol.

The above-described properties of sitosterol-*d*-glucoside closely resemble those of the naturally occurring phytosterolins, and it is evident that the substances previously designated ipuranol, cluytianol, and trifolianol consist almost entirely of sitosterol-*d*-glucoside.

### II. *Cholesterol*-d-*glucoside*, $C_{27}H_{45}O\cdot C_6H_{11}O_5$.

The cholesterol employed in the preparation of the above glucoside melted at 146—147°, gave on analysis results agreeing with the formula $C_{27}H_{46}O$, and possessed an optical rotation of $[\alpha]_D$ −40·3° ($c$=2·1 in chloroform).

Five grams of cholesterol and 5 grams of bromoacetoglucose, dissolved in ether, were shaken for eight hours in the presence of dry silver oxide, and the product of the reaction was examined in the manner described in connexion with the preparation of sitosterol-*d*-glucoside. The cholesterol-*d*-glucoside thus obtained was purified by crystallisation from dilute pyridine, when it was deposited in minute, colourless needles, which began to soften about 270°, and completely melted at 285°. The yield of glucoside amounted to 2 grams:

0·0704 gave 0·1864 $CO_2$ and 0·0651 $H_2O$. C=72·2; H=10·3.

$C_{33}H_{56}O_6$ requires C=72·3; H=10·2 per cent.

The properties of cholesterol-*d*-glucoside are very similar to those of sitosterol-*d*-glucoside. It is very sparingly soluble in alcohol, chloroform, or ether, but readily so in pyridine or hot amyl alcohol. It yields the characteristic cholesterol colour reactions.

*Tetra-acetylcholesterol*-d-*glucoside*, $C_{27}H_{45}O\cdot C_6H_7O_5Ac_4$.—This substance was obtained by heating the glucoside with acetic anhydride for half an hour. On removing the greater part of the latter and adding alcohol to the residue, a crystalline acetyl derivative was deposited, which was recrystallised from alcohol, and obtained in colourless needles, melting at 159—160°:

0·0882 gave 0·2222 $CO_2$ and 0·0707 $H_2O$. C=68·7; H=8·9.

$C_{41}H_{64}O_{10}$ requires C=68·7; H=8·9 per cent.

0·1822, made up to 20 c.c. with chloroform, gave $\alpha_D$ −0°26′ in a 2-dcm. tube, whence $[\alpha]_D$ −23·8°.

### III. *Myricyl*-d-*glucoside*, $C_{30}H_{61}O \cdot C_6H_{11}O_5$.

Five grams of myricyl alcohol were shaken for eight hours with a dry ethereal solution of bromoacetoglucose (5 grams) in the presence of dry silver oxide (5 grams). The mixture was then filtered, the filtrate evaporated, and the solid residue, which contained the desired tetra-acetylmyricyl-*d*-glucoside mixed with unchanged myricyl alcohol, was dissolved in a mixture of equal parts of hot benzene and alcohol. On cooling, the greater part of the myricyl alcohol separated and was collected, whilst the tetra-acetyl derivative of the glucoside remained in the filtrate. The latter was subsequently heated for a very short time (about one minute) with an excess of alcoholic potassium hydroxide, and the glucoside, which separated on cooling, collected and washed with cold alcohol. It was purified by dissolving in hot chloroform and precipitating the glucoside from solution by the addition of ether. This product was then crystallised from hot alcohol, when it separated in small, colourless plates, melting at 99°. The yield of pure glucoside amounted to about 10 per cent. of the myricyl alcohol employed in the reaction:

0·1000 gave 0·2642 $CO_2$ and 0·1078 $H_2O$. $C=72·1$; $H=12·0$.

$C_{36}H_{72}O_6$ requires $C=72·0$; $H=12·0$. per cent.

*Myricyl*-d-*glucoside* is insoluble in water, sparingly soluble in ether or chloroform, but readily so in pyridine or hot alcohol. It could only be obtained in one modification, thus differing from the glucoside of ceryl alcohol.

*Tetra-acetylmyricyl*-d-*glucoside*, $C_{30}H_{61}O \cdot C_6H_7O_5Ac_4$.—This compound was obtained by heating the glucoside with acetic anhydride for some time, then removing the greater portion of the latter by distillation and adding alcohol to the residue. The precipitate of acetyl derivative thus obtained was crystallised from a mixture of ethyl acetate and alcohol, when it separated in small, colourless leaflets, melting at 78—79°:

0·1010 gave 0·2533 $CO_2$ and 0·0972 $H_2O$. $C=68·4$; $H=10·7$.

$C_{44}H_{80}O_{10}$ requires $C=68·6$; $H=10·5$ per cent.

0·1542, made up to 20 c.c. with chloroform, gave $\alpha_D$ $-0°10'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-10·8°$.

Tetra-acetylmyricyl-*d*-glucoside is readily soluble in ether, chloroform, or benzene, but only sparingly so in cold alcohol.

### IV. *Ceryl*-d-*glucoside*, $C_{27}H_{55}O \cdot C_6H_{11}O_5$.

The preparation and isolation of this compound were effected in a manner precisely similar to that adopted in the preparation of myricyl-*d*-glucoside. The glucoside was obtained, after being crystallised from methyl alcohol, in small, hexagonal plates, melting at 94°. The yield of pure substance amounted to about 10 per cent. of the ceryl alcohol employed:

0·1460 gave 0·3808 $CO_2$ and 0·1560 $H_2O$. C=71·1; H=11·9.

$C_{33}H_{66}O_6$ requires C=71·0; H=11·8 per cent.

*Ceryl*-d-*glucoside* was found to exist in two modifications, the one melting at 94°, as described above, whilst the other melts at 135°. The latter was obtained by dissolving the former in hot chloroform, when glistening leaflets of the modification of high melting point immediately separated from the hot solution. If the latter is recrystallised from alcohol, it is more or less transformed into the modification of lower melting point. The glucoside melting at 135° was analysed, with the following result:

0·0871 gave 0·2263 $CO_2$ and 0·0928 $H_2O$. C=70·9; H=11·8.

$C_{33}H_{66}O_6$ requires C=71·0; H=11·8 per cent.

*Tetra-acetylceryl*-d-*glucoside*, $C_{27}H_{55}O \cdot C_6H_7O_5Ac_4$.—This compound was prepared in the manner described in connexion with the preparation of tetra-acetylmyricyl-*d*-glucoside. It crystallised from a mixture of alcohol and ethyl acetate in small, colourless leaflets, melting at 85—87°:

0·0758 gave 0·1883 $CO_2$ and 0·0696 $H_2O$. C=67·8; H=10·2.

$C_{41}H_{74}O_{10}$ requires C=67·8; H=10·2 per cent.

0·2010, made up to 20 c.c. with chloroform, gave $\alpha_D$ −0°17′ in a 2-dcm. tube, whence $[\alpha]_D$ −14·1°.

### V. *Cetyl*-d-*glucoside*, $C_{16}H_{33}O \cdot C_6H_{11}O_5$.

This glucoside has already been described by Fischer and Helferich (*loc. cit.*). In the present investigation it was prepared by the method of these authors, but a more expeditious way of isolating the product was adopted. Five grams of cetyl alcohol were shaken for eight hours in dry ethereal solution with bromoacetoglucose (5 grams) and dry silver oxide (5 grams). The mixture was then filtered to remove the silver, the ethereal filtrate evaporated, and the residue from the latter hydrolysed in alcoholic solution by heating for about a minute with an excess of potassium hydroxide. Water was then added to the alcoholic liquid, and the precipitated solid extracted with ether. On washing the ethereal solution with water and thus removing the alcohol contained in it, the glucoside separated as a flocculent precipitate, which was collected and crystallised from chloroform. It was thus obtained in small, colourless needles, which began to soften at 78°, and completely melted at about 150°. It yielded an acetyl derivative, melting at 71—73°, and was thus found to possess the properties previously ascribed to it. The glucoside could not be separated into modifications of definite melting point as in the case of ceryl-*d*-glucoside.

*Tetrabenzoylcetyl*-d-*glucoside*, $C_{16}H_{33}O \cdot C_6H_7O_5Bz_4$.—This derivative of cetyl-*d*-glucoside, not hitherto described, was prepared by heating the glucoside with benzoyl chloride for a few minutes in the presence of pyridine. On adding alcohol and keeping the mixture for some time, the benzoyl compound separated in clusters of silky needles, melting at 65°:

0·0969 gave 0·2600 $CO_2$ and 0·0653 $H_2O$. C=73·2; H=7·3.

$C_{50}H_{60}O_{10}$ requires C=73·2; H=7·2 per cent.

0·2380, made up to 20 c.c. with chloroform, gave $\alpha_D$ +0°22′ in a 2-dcm. tube, whence $[\alpha]_D$ +15·4°.

Tetrabenzoylcetyl-*d*-glucoside is readily soluble in ether, chloroform, or benzene, but dissolves sparingly in alcohol.

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# CIX.—*Oxidation of Sphingosine and the Isolation and Purification of Cerebrone.**

By ARTHUR LAPWORTH.

SPHINGOSINE was isolated from decomposition products of brain-lipoids by Thudichum ("Die chemische Constitution des Gehirns," Tübingen, 1901), and its relations to one of these, namely, "cerebrone," was established by the work of Thierfelder and his pupils, who showed that the latter compound undergoes hydrolysis with acids, yielding molecular proportions of galactose, cerebronic acid, and sphingosine:

$$C_{48}H_{93}O_9N + 4H_2O = C_6H_{12}O_6 + C_{25}H_{50}O_3 + C_{17}H_{35}O_2N.$$

Cerebronic acid was recognised as a hydroxycarboxylic acid, whilst sphingosine proved to be a mono-acidic base, yielding stable salts with mineral acids (Thierfelder, *Zeitsch. physiol. Chem.*, 1904, **43**, 21; 1905, **44**, 366; Kitawaga and Thierfelder, *ibid.*, 1906, **49**, 286).

Between 1906 and the end of 1911 nothing of note was published dealing with the chemistry of cerebronic acid or sphingosine, and in 1910 the author was asked by Prof. Lorrain Smith to assist in his studies of brain-lipoids, in connexion with the question of the processes of fatty degeneration (compare Lorrain Smith and Mair, *J. Path. Bact.*, 1910, **15**, 122; 1911, **16**, 131; also Lapworth, *ibid.*, 1911, **16**, 255). The method described by Lorrain Smith and Mair for the quantitative isolation of cerebrone from chloroform extract of brain was examined by the author with the object of preparing this lipoid on a large scale and simultaneously investigating the exact nature of cerebronic acid and sphingosine. Having corroborated the more important points established by Thierfelder, the author proceeded, in conjunction with Prof. W. H. Perkin, to investigate the constitution of cerebronic acid; the latter compound was analysed, its methyl ester prepared and purified and the percentage of methoxyl determined by Zeisel's method, with results entirely in harmony with Thierfelder's conclusions. Simultaneously the author was examining the properties of sphingosine, and in particular its behaviour towards oxidising agents, and observed that the base was converted by boiling nitric acid into a variety of products, including succinic acid and a mixture of acids having the properties of those of the fatty series, some being readily, and others but slightly volatile in steam. Suspecting that most of these were secondary products, attempts were made to isolate the highest of these by the use of a mild oxidising agent, and partial success was met with when chromic acid was used, it being observed that the acid product was free from the more volatile constituents formerly present.

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* Abstracts, P., 1913, **29**, 154, 175.

At this juncture the papers by Levene and Jacobs (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxix) and by Thomas and Thierfelder appeared (*Zeitsch. physiol. Chem.*, 1912, **77**, 202). The first-named authors practically established the character of sphingosine as a dihydroxy-derivative of a primary, unsaturated amine; Thomas and Thierfelder confirmed by independent observations the fact that sphingosine yielded a triacetyl derivative. A request was tendered by Thierfelder to be allowed for some years to work in sole possession of the field of investigation of the brain-cerebrosides, but to this Levene and Jacobs, with considerable reason, did not accede.

The experiments in the author's and Prof. Perkin's laboratories were for the most part abandoned temporarily, in view of the considerable strides made by Levene and Jacobs and by Thierfelder, and it was decided for the time being simply to complete the practical modifications of Lorrain Smith and Mair's method of cerebrone-extraction on a large scale and to identify the fatty acid of highest molecular weight present in the oxidation mixture from cerebrone, and of which no mention had so far been made in any publication by other workers.

### *Preparation of Pure Cerebrone on a Large Scale.*

The fresh brain is partly dried by soaking in spirit, and, when firm, is passed through a mincing machine and exhaustively extracted with boiling methyl alcohol. The alcoholic extracts, with any material they may deposit, are united, and solvent removed by distillation until they contain about 5—10 per cent. of residue not volatile at 100°, when about 0·5 gram of solid phenolphthalein per litre is added. A cold saturated solution of barium hydroxide in methyl alcohol is very slowly dropped into the boiling liquid until the latter assumes a faint red colour, indicative of alkalinity, and permanent for half an hour; this results in the deposition of much phosphatic material as a viscid, coherent mass, the presence of which renders the subsequent operations difficult (compare Lapworth, *J. Path. Bact.*, 1911, **15**, 255) and therefore the supernatant solution is finally decanted into another flask, the small quantity of cerebrone which is retained in the viscid residue being extracted, if necessary, with successive small quantities of boiling methyl alcohol.

The united methyl-alcoholic liquors, if allowed to cool, deposit a white, easily filterable mass, consisting of cholesterol, mixed with cerebrone which obstinately retains phosphatides. These phosphatides cannot, in the author's experience, be removed by any process other than hydrolysis. Having tried hydrolysis with aqueous baryta and found it unsatisfactory from the point of view of simplicity in manipulation on a large scale, and destructive of much cerebrone when prolonged, as appears usually necessary, the author has based his subsequent procedure on the observations of Lorrain Smith and Mair (*J. Path. Bact.*, 1910, **15**, 122; 1911, **16**, 131), which were published prior to the paper of Loening and Thierfelder, who also advocated the use of boiling acetone as purifying agent (*Zeitsch. physiol. Chem.*, 1912, **77**, 202, *et seq.*), but had evidently overlooked the earlier work.

The decanted liquor and washings are raised once more to boiling, and finely powdered barium oxide or hydroxide is shaken in, every precaution being taken to avoid the formation of clots protecting the oxide; in all, 1 gram of BaO is used for every 6 grams of residue not volatile at 100° previously estimated to be present in the original alcoholic extract. The boiling is continued for ten to twelve hours, when the bulk of the solvent is removed by distillation. To the still moist residue in the flask is added a mixture of equal volumes of chloroform and methyl alcohol (5 c.c. of this mixture for every gram of "residue not volatile at 100°"), and a pinch of solid phenolphthalein, the whole raised to boiling, glacial acetic acid added drop by drop until all trace of red colour in solution and solid has been discharged; the mixed solvent is then removed by distillation.

Cerebrone and cholesterol are now easily freed from sparingly soluble phosphatic acids and barium salts by extraction and recrystallisation from hot methyl alcohol, filtration being resorted to only at the beginning and the end of these operations; the first-named substances are then separated from one another by extraction with ether, when the cerebrone remains undissolved.

If phosphatides are still present in the cerebrone, the latter may be subjected to continuous extraction with boiling acetone, as recommended by Lorrain Smith and Mair (*loc. cit.*), but if the addition of the powdered baryta has been made so cautiously as to avoid the formation of lumps at the beginning of the hydrolysis, only traces of phosphatide will be found.

It may be worth while to state that the author has never observed cerebrone in a solid-crystalline form, although many specimens presented that appearance both to the naked eye and when examined with a microscope in polarised light with crossed nicols. As is also the case with sphingosine, very thin, plate-like forms often separate; these are birefringent, and bend in straight folds, thus producing the appearance of needles, especially in polarised light. In every case, however, the dry material, when heated, gradually became less firm, and finally quite fluid, no break being observed until the birefringence and viscosity of the fluid-crystalline substance disappeared at about 200°, so that the so-called "melting point" is only the clearing point of the opalescent "crystalline" fluid. This is but a corroboration and extension of the conclusions of Lorrain Smith and Mair (*Proc. Path. Soc.*, 1910, 8), who were the first to recognise the fluid-crystalline characters of cerebrone and sphingosine as they usually appear, and the true character of the so-called melting point of cerebrone. The author has had the advantage of their experience and advice in his observations on the nature of the seeming crystals of these two compounds, and the facts are worthy of wider attention than they appear to have received.

### *Preparation of Sphingosine.*

Cerebrone, prepared as above, and free from phosphorus, was hydrolysed by hot 3 per cent. aqueous hydrochloric acid for twenty-four hours. The resulting insoluble mixture of cerebronic acid and sphingosine hydrochloride was rapidly washed with water, then dissolved in hot methyl alcohol, and mixed with excess of a saturated solution of sodium hydroxide in the same solvent. Sodium cerebronate separated on cooling, and was removed by filtration, the filtrate diluted with four times its bulk of water and extracted with ether; the latter was washed several times with water containing 15 per cent. of methyl alcohol, evaporated and dried at 100°. The residue, which was mainly sphingosine, was extracted with cold spirit, the resulting clear solution nearly neutralised with sulphuric acid, and the precipitated sphingosine sulphate crystallised from alcohol.

### *Oxidation of Sphingosine.*

Sphingosine sulphate, prepared and purified as above, was dissolved in glacial acetic acid and cautiously oxidised with successive small quantities of chromium trioxide at the lowest temperature required to cause slight effervescence; oxidation was completed with excess of trioxide at 100°, when the liquid was diluted with water, and excess of chromium trioxide reduced by a stream of sulphur dioxide. A current of steam was then used to remove most of the acetic acid, the receiver being changed when solid matter appeared in the condenser. The first portions of solid which passed over were collected, dried, and distilled in a vacuum, and were found to melt at 38·5—40°.

As distillation of the acid slackened, the green liquid in the flask was cooled, extracted with ether, and the latter evaporated. A green residue was obtained, which was decomposed readily by concentrated hydrochloric acid, yielding a green solution and a white solid, which was found to be identical with the volatile acid, and had evidently been retained as chromium salt.

Unfortunately some of the acid was lost before the total weight was determined, but the yield would evidently have been considerable, and 2·3 grams were finally isolated in purified state from 8 grams of sphingosine sulphate.

### *Identification of the Acid.*

The collected acid was dried and distilled; it boiled constantly at 136—137/100 mm., and successive small fractions of the distillate all melted between 38·5 and 40·5°:

0·2790 gave 0·7440 $CO_2$ and 0·3020 $H_2O$. C = 72·7; H = 12·0.

$C_{13}H_{26}O_2$ requires C = 72·8; H = 12·2 per cent.

For the determination of its equivalent, a solution of sodium in methyl alcohol was standardised by means of pure stearic acid, with litmus as indicator. 0·2620 Gram of stearic acid required 10·45 c.c., whilst 0·1302 gram of the acid under examination required 6·90 c.c., under precisely similar conditions, to yield a solution with the same tint. The equivalent of the acid was therefore 212, that required for a monobasic acid, $C_{13}H_{36}O_2$, being 214.

As these properties were very similar to those attributed to *n*-tridecylic acid, a sample of the latter was made from myristic acid by converting the latter in its α-bromo- and α-hydroxy-derivative successively and oxidising the latter with potassium permanganate in acetone. The product was identical in all respects with the acid obtained from sphingosine, and had no influence on its melting point. The substances, separately or mixed, presented, on a slide beneath a cover slip, precisely the same appearance when fused and allowed to solidify, forming clear areas with sharply defined edges; in all three cases, too, the materials when examined in convergent polarised light exhibited in most regions one axis of a biaxial interference figure emerging obliquely and at apparently the same angle to the normal.

In view, however, of the general tendency of fatty acids to form mixed crystals, thus rendering complete identification less simple than usual, a sample of the acid from sphingosine was brominated in a closed tube in presence of phosphorus pentachloride, the product decomposed by boiling with anhydrous formic acid and the α-bromo-derivative crystallised from the same solvent. A portion of this α-bromo-acid was next converted by Le Sueur's method (T., 1905, **87**, 1905) into the α-hydroxy-acid. This bromo-compound and the hydroxy-acid melted at 29·5—30° and at 76—77° respectively, whilst Le Sueur (*loc. cit.*, *et seq.*) gives 30·5° and 78° respectively for the corresponding derivatives of tridecylic acid, an agreement which, considering the small quantity of acid brominated (less than 1 gram), was sufficiently close fully to establish the identity of the oxidation product of sphingosine as tridecylic acid.

Whilst it is obvious that much experimental work remains to be done before the exact constitution of sphingosine is established, yet it would seem probable, having regard to the fact that straight carbon chains are characteristic of most of the simpler brain substances that the complex:

$$CH_3\cdot[CH_2]_{11}\cdot\underset{(5)}{\dot{C}H}\cdot\underset{(4)}{\dot{C}H}\cdot\underset{(3)}{\dot{C}H}\cdot\underset{(2)}{\dot{C}H}\cdot\underset{(1)}{\dot{C}H_2},$$

is present in this base.

Evidence as to the position of the ethylenic linking should be obtainable by examining the oxidation products of Levene and Jacob's dihydrosphingosine. If, for example, the double linking unites the atoms numbered (4) and (5), then oxidation of the reduced base should furnish *n*-quindecylic acid, and doubtless these workers will be able to decide this question.

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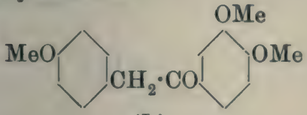
# CX.—*Synthesis of Unsymmetrical Derivatives of Deoxybenzoin.*

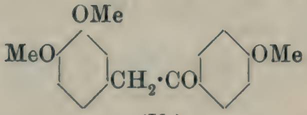
By JOHN CANNELL CAIN, JOHN LIONEL SIMONSEN, and CLARENCE SMITH.

IN a recent paper (Cain and Simonsen, T., 1912, **101**, 1061) it was shown that santalin dimethyl ether, $C_{17}H_{18}O_5$, on oxidation with potassium permanganate, yields a mixture of anisic and veratric acids, and it appeared to be of interest therefore in connexion with the elucidation of the constitution of santalin, to synthesise a series of compounds which might be expected to furnish the above acids on oxidation.

In the present paper is described the synthesis of two trimethoxydeoxybenzoins:



(I.)



(II.)

The starting point for the preparation of *β-keto-α-4-methoxyphenyl-β-3:4-dimethoxyphenylethane* (I) was *p*-methoxyphenylpyruvic acid (Dakin, *J. Biol. Chem.*, 1910, **8**, 17; Wakeman and Dakin, *ibid.*, 1911, **9**, 150), which on oxidation with hydrogen peroxide yielded *p*-methoxyphenylacetic acid, $OMe\cdot C_6H_4\cdot CH_2\cdot CO_2H$; the *chloride* of this when condensed with veratrole by means of aluminium chloride, gave the desired substance (I).

The substituted deoxybenzoin obtained in this way gives with hydroxylamine an *oxime*, $OMe\cdot C_6H_4\cdot CH_2\cdot C(:NOH)\cdot C_6H_3(OMe)_2$, and when the latter is treated with phosphorus pentachloride, p-*methoxyphenylaceto*-3:4-*dimethoxyanilide*,

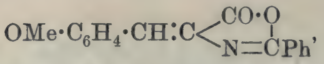
$$MeO\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH\cdot C_6H_3(OMe)_2,$$

is produced.

By a similar series of reactions *β-keto-β-4-methoxyphenyl-α-3:4-dimethoxyphenylethane* (II) was obtained. 3:4-Dimethoxyphenylpyruvic acid (Kropp and Decker, *Ber.*, 1909, **42**, 1184) was oxidised to 3:4-dimethoxyphenylacetic acid, the chloride of which was condensed with anisole to the required compound (II) of which the *oxime* was prepared.

## EXPERIMENTAL.

### *β-Keto-α-4-methoxyphenyl-β-3:4-dimethoxyphenylethane* (I).

*p*-Methoxyphenylpyruvic acid, $OMe\cdot C_6H_4\cdot CH_2\cdot CO\cdot CO_2H$, was prepared by heating the lactone of α-benzoylamino-*p*-methoxy-cinnamic acid,  $\mathrm{OMe\cdot C_6H_4\cdot CH{:}C}\Big\langle\begin{array}{l}\mathrm{CO\cdot O}\\ \mathrm{N{=}CPh}\end{array}$, with aqueous potassium hydroxide, as described by Wakeman and Dakin (*loc. cit.*), but the acid was isolated in a different manner from that adopted by these authors.

The lactone (55 grams) was mixed with potassium hydroxide (64 grams) in water (600 c.c.), and heated on the sand-bath under reflux until no further odour of ammonia could be detected (about five hours). The liquid was cooled, acidified, and the oily mixture of acids extracted with ether. In order to separate the benzoic and pyruvic acids, the mixture was esterified and fractionally distilled under 15 mm. pressure. After the ethyl benzoate had passed over, the temperature rose rapidly, and *ethyl* p-*methoxyphenylpyruvate* distilled with considerable decomposition at about 190°. For identification it was converted into its *semicarbazone*, which separated from alcohol in colourless needles, melting at 152—153°:

0·1108 gave 16·0 c.c. $N_2$ at 32° and 753 mm. $N=15·4$.

$C_{13}H_{17}O_4N_3$ requires $N=15·1$ per cent.

In order to obtain the free acid the ester (5 grams) was hydrolysed on the water-bath with alcoholic potassium hydroxide (3 grams KOH), the alcohol removed, and, on acidifying, the acid separated as a semi-solid mass. This was ground with hot benzene, which removed the coloured impurity, leaving the acid as a chalky, white mass. After crystallisation from a mixture of ethyl acetate and benzene, the properties of the acid agreed with those described by Wakeman and Dakin.

*Preparation of* p-*Methoxyphenylacetic Acid.*—In order to prepare this acid, the mixture of benzoic acid and *p*-methoxyphenylpyruvic acid was not isolated, but was directly oxidised by hydrogen peroxide in the following manner.

The alkaline solution of the acids obtained by the hydrolysis of the lactone (90 grams) with potassium hydroxide was extracted with ether to remove a trace of oily impurity, and treated gradually with hydrogen peroxide (30 c.c. of "perhydrol" diluted with 300 c.c. of water). The oxidation takes place rapidly, and the solution was kept well cooled. After remaining overnight the solution was filtered and acidified, the mixture of acids extracted with ether, and the latter were converted into their esters in the usual manner. On distilling under 7 mm. pressure, ethyl benzoate passed over first, and then *ethyl* p-*methoxyphenylacetate*, which was readily obtained pure, and boiled at 138—140° (yield, 30 grams). On hydrolysis, *p*-methoxyphenylacetic acid was isolated in iridescent plates, melting at 85—87°.

When *p*-methoxyphenylacetic acid is treated with phosphorus pentachloride, it is converted into its *chloride*, which is an oil having an odour like that of benzoyl chloride and boiling at 143°/10 mm.:

0·1868 gave 0·1496 AgCl. Cl = 19·4.

$C_9H_9O_2Cl$ requires Cl = 19·2 per cent.

*p*-Methoxyphenylacetyl chloride (10 grams) was dissolved in carbon disulphide (50 c.c.), and after the addition of veratrole (15 grams), aluminium chloride (15 grams) was slowly added. When the vigorous reaction which took place had subsided, the mixture was heated on the water-bath for three hours. The deep red aluminium compound which had separated was decomposed in the usual manner, and the carbon disulphide and unchanged veratrole were removed by means of steam. On cooling, the trimethoxydeoxybenzoin (I) separated as a reddish-brown, crystalline mass. It was collected, well washed with sodium carbonate solution and water, and purified by crystallisation from alcohol, from which it separates in bunches of slender needles, melting at 118°:

0·1657 gave 0·4308 $CO_2$ and 0·0935 $H_2O$. C = 70·9; H = 6·3.
0·1372 „ 0·4308 $CO_2$ „ 0·0818 $H_2O$. C = 71·1; H = 6·6.

$C_{17}H_{18}O_4$ requires C = 71·3; H = 6·3 per cent.

*β-Keto-α-4-methoxyphenyl-β-3:4-dimethoxyphenylethane* (I) is readily soluble in benzene, ethyl acetate, chloroform, or hot alcohol, but only sparingly so in light petroleum or cold alcohol. It gives no colour with ferric chloride. When treated with bromine, substitution readily takes place, but a mixture of bromo-derivatives seems to be formed, and so far no crystalline compound has been isolated.

The *oxime*, $OMe\cdot C_6H_4\cdot CH_2\cdot C(:NOH)\cdot C_6H_3(OMe)_2$, was readily obtained when the trimethoxybenzoin was dissolved in alcohol and heated with an alcoholic solution of hydroxylamine hydrochloride and potassium hydroxide on the water-bath for some hours. On pouring into water an oil separated, which rapidly solidified. For analysis it was crystallised from alcohol, from which it separated in well-developed prisms, melting at 143°:

0·1207 gave 0·2984 $CO_2$ and 0·0690 $H_2O$. C = 67·4; H = 6·3.

$C_{17}H_{19}O_4N$ requires C = 67·8; H = 6·3 per cent.

A careful examination of the mother liquors showed that not a trace of the isomeric oxime was formed.

When this oxime, dissolved in a mixture of benzene and ether, was treated with phosphorus pentachloride in the usual manner, the Beckmann rearrangement took place, and p-*methoxyphenylaceto-3:4-dimethoxyanilide*, $MeO\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH\cdot C_6H_3(OMe)_2$, was formed. This was isolated in the usual manner, and purified by crystallisation from alcohol, when it separated in prismatic needles, melting at 147—148°:

0·1204 gave 6·0 c.c. $N_2$ at 33° and 763 mm. N = 5·3.

$C_{17}H_{19}O_4N$ requires N = 4·6 per cent.

When hydrolysed with concentrated hydrochloric acid, the anilide yielded *p*-methoxyphenylacetic acid and veratrylamine (m. p. 80—82°; platinichloride, yellow needles, m. p. 227—228°).

### *β-Keto-β-4-methoxyphenyl-α-3 : 4-dimethoxyphenylethane* (II).

The alkaline solution resulting from the hydrolysis of the lactone of *α*-benzoylamino-3 : 4-dimethoxycinnamic acid and containing 3 : 4-dimethoxyphenylpyruvic acid (Kropp and Decker, *loc. cit.*) was gradually treated with 200 c.c. of 3 per cent. hydrogen peroxide, the flask being cooled by water during the oxidation. After keeping for about twenty hours, the pale yellow solution was filtered and acidified. The pasty mixture of acids thus obtained was extracted with ether, and the crude acids (54 grams) remaining after evaporation of the ether were esterified in the usual manner. The mixture of esters was isolated and fractionated under diminished pressure. After ethyl benzoate had distilled over at 117—120°/48 mm., the temperature rose rapidly, and *ethyl* 3 : 4-*dimethoxyphenylacetate* passed over at 199—200°. By redistillation the ester (15 grams) was obtained as a colourless liquid, boiling at 191°/25 mm.

3 : 4-Dimethoxyphenylacetic acid was obtained by hydrolysing the ester with alcoholic potassium hydroxide. Its properties corresponded with those given by Pictet and Finkelstein (*Ber.*, 1909, **42**, 1984).

3 : 4-Dimethoxyphenylacetyl chloride (Pictet and Finkelstein, *loc. cit.*, p. 1985) was dissolved in 70 c.c. of dry carbon disulphide, 20 grams of anisole were added, and the mixture was treated slowly with 20 grams of aluminium chloride. A vigorous reaction soon commenced, which was moderated by cooling the flask in water. When the reaction had subsided, the mixture was heated on the water-bath for four hours. Ice and ice-cold water were then gradually added to the cooled mixture, which was well shaken and treated with 10 c.c. of concentrated hydrochloric acid. The reddish-black additive compound slowly decomposed, yielding a yellowish-brown solid. After the carbon disulphide and excess of anisole had been removed by means of steam, the reddish-brown residue was collected, washed with water, and ground twice with *N*-potassium hydroxide. The yellow residue (11 grams) was separated from the dark red solution, washed with water, dried in a vacuum, and crystallised twice from 96 per cent. alcohol and once from benzene.

The product of the reaction was thus obtained in colourless needles (4·5 grams), melting at 138°:

0·3153 gave 0·8238 $CO_2$ and 0·1760 $H_2O$. C = 71·3; H = 6·2.
$C_{17}H_{18}O_4$ requires C = 71·3; H = 6·3 per cent.

*β-Keto-β-4-methoxyphenyl-α-3*: *4-dimethoxyphenylethane* is extremely soluble in boiling benzene, and readily so in boiling 96 per cent. alcohol; in the cold solvents it is only sparingly soluble. It does not develop a coloration with concentrated alcoholic sodium hydroxide, but dissolves in concentrated sulphuric acid with a yellow colour.

The *oxime*, $C_6H_3(OMe)_2{\cdot}CH_2{\cdot}C(\colon NOH){\cdot}C_6H_4{\cdot}OMe$, was prepared by treating 0·71 gram of the substance just described, dissolved in 50 c.c. of 96 per cent. alcohol, with three equivalents of hydroxylamine hydrochloride and an excess (2 grams) of sodium hydroxide dissolved in water. After the mixture had been heated on the water-bath for two hours, the alcohol was removed by distillation, water was added to the residue, which was then acidified with dilute sulphuric acid. The precipitate was extracted with ether, the ether evaporated, and the oily residue, after two crystallisations from 96 per cent. alcohol, was obtained in colourless needles, melting at 100—101°:

0·1316 gave 5·2 c.c. $N_2$ at 20° and 776 mm. N = 4·7.
$C_{17}H_{19}O_4N$ requires N = 4·6 per cent.

The authors express their thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the expense of the above investigation.

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## CXI.—*The Estimation of Small Quantities of Lead.*

By Alfred Vincent Elsden and John Firth Stansfield.

Wilkie (*J. Soc. Chem. Ind.*, 1909, **28**, 636) states that lead in presence of a sufficiency of ferric iron is completely precipitated by ammonia. This has been confirmed, and it occurred to the authors that this property might form a convenient method for the separation and estimation of lead in small quantities in solution, since, having concentrated the lead in the precipitate of ferric hydroxide, it only remains to separate the two metals. After solution of the precipitate in acid, the separation could, of course, be effected either by means of hydrogen sulphide or by evaporation with sulphuric acid, but a more rapid and equally accurate method has been devised.

It was at first hoped to effect the separation by precipitation of the iron in acid solution either as basic acetate or as basic formate, but many experiments under varying conditions of acidity, concentration, etc., have shown that a satisfactory separation of iron from lead cannot be obtained by this means. It was found that the more acid the solution the more complete was the separation, but eventually a point was reached when the solution was too acid for the complete precipitation of the iron, whilst the iron precipitate still carried down some lead.

Attention was then given to the precipitation of lead as molybdate. Brearley (*Chem. News*, 1898, **78**, 203), and later Brearley and Ibbotson ("Analysis of Steel Works Materials"), give some details of the precipitation of lead as molybdate, but with reference to quantities larger in general than those contemplated by the present authors. It was ascertained that even quantities as small as 2 or 3 milligrams of lead in a volume of 50 to 100 c.c. of solution could be accurately precipitated and weighed as molybdate, as will be seen from the following results, the lead being dissolved in about 75 c.c. of solution:

| Lead added. | Lead found. |
|---|---|
| 0·0252 | 0·0254 |
| 0·0030 | 0·0029 |
| 0·0020 | 0·0021 |

In the presence of ferric iron lead cannot be estimated as molybdate directly, since free mineral acid interferes with the precipitation, and in weak acetic acid solution iron will be co-precipitated.

The authors have found, however, that if the iron is first reduced to the ferrous condition the lead can be precipitated directly as molybdate in weak acetic acid solution without precipitation of iron, and this even when the iron is in relatively very much larger quantity than the lead. A single precipitation usually gives too high a result, but by redissolving and reprecipitating the lead molybdate the results are satisfactory, as the figures on p. 1041 show.

The detailed procedure for the estimation of small quantities of lead in solution is as follows.

To the solution is added at least ten times as much iron (as ferric chloride solution of known concentration) as there is likely to be lead present. After mixing thoroughly, ammonia is added in excess, and the solution boiled and filtered. The precipitate is

| Iron added. | Lead added. | Lead found. | Ratio Fe : Pb. |
|---|---|---|---|
| 0·1000 | 0·0010 | 0·0011 | 100 : 1 |
| 0·0600 | 0·0020 | 0·0022 | 30 : 1 |
| 0·1000 | 0·0020 | 0·0022 | 50 : 1 |
| 0·1000 | 0·0020 | 0·0022 | 50 : 1 |
| 0·1000 | 0·0030 | 0·0030 | 33 : 1 |
| 0·1000 | 0·0040 | 0·0042 | 25 : 1 |
| 0·1000 | 0·0040 | 0·0041 | 25 : 1 |
| 0·1000 | 0·0050 | 0·0052 | 20 : 1 |
| 0·2000 | 0·0060 | 0·0061 | 33 : 1 |
| 0·1500 | 0·0070 | 0·0071 | 21 : 1 |
| 0·1500 | 0·0080 | 0·0083 | 19 : 1 |
| 0·2000 | 0·0100 | 0·0102 | 20 : 1 |

dissolved in 10—20 c.c. of hot concentrated hydrochloric acid, and the filter washed thoroughly with boiling water until the combined filtrate and washings reach a volume of about 75 c.c. Ammonia is then added to the solution, conveniently from a burette, until a slight permanent precipitate is produced. *N*/2-Hydrochloric acid is then added to the extent of 2 c.c. for every 0·0100 gram of iron used, with a minimum of 10 c.c.; 0·2 gram of sodium sulphite crystals are then added for every 0·0100 gram of iron, with a minimum of 1 gram, and the solution warmed until reduction is effected. Without boiling off the excess of sulphur dioxide, 10—20 c.c. of ammonium acetate solution (10 per cent.) are added, the solution heated to the boiling point, and finally 10—20 c.c. of ammonium molybdate solution (5 per cent.) are added slowly and with agitation of the liquid. After boiling for a short time the precipitate is filtered rapidly through a close textured paper, and washed two or three times with boiling water.

The precipitate is dissolved from the paper in 10 c.c. of hot concentrated hydrochloric acid, and the paper washed thoroughly with boiling water to a total volume of not more than 50 c.c. A few drops of tartaric acid solution (5 per cent.) and litmus solution are added, after which concentrated ammonia is added from a burette until the liquid is neutral. The solution is then acidified with a few drops of *N*/2-hydrochloric acid, and, after addition of a few c.c. of ammonium acetate solution, boiled for a short time. The precipitate is collected, washed with hot water, ignited with the paper, and weighed.

With regard to the influence of the presence of other elements on the precipitation of lead molybdate, Brearley (*loc. cit.*) has shown that a large number of metals do not interfere if certain precautions are taken. The present authors have investigated the influence of tin, antimony, and phosphorus on the procedure described above. If present in solution with the lead they are largely, if not completely, carried down by the iron precipitate. The method of dealing with the mixed precipitate has then to be modified, and it is desirable to separate the iron and the phosphorus by means of hydrogen sulphide in hydrochloric acid solution. The tin and antimony are then separated from the lead by means of ammonium sulphide in the usual manner. The remaining lead sulphide may be conveniently dissolved in hydrochloric acid containing bromine, and estimated as molybdate as already described. The following results were thus obtained:

| Iron added. | Tin added. | Antimony. added. | Phosphorus added. | Lead added. | Lead found. |
|---|---|---|---|---|---|
| 0·0500 | 0·0050 | 0·0050 | 0·0050 | 0·0040 | 0·0042 |
| 0·0500 | 0·0050 | 0·0050 | 0·0050 | 0·0050 | 0·0052 |
| 0 0500 | 0·0050 | 0·0050 | 0·0050 | 0·0060 | 0 0062 |

The authors believe that this method of separation and estimation of lead will be found capable of wide application, especially in those cases where small amounts of lead have to be separated from solution.

It may also be applied to the estimation of lead in many non-ferrous alloys, and in such cases, when the amount of lead is small, it has advantages as to speed and accuracy over the usual method of evaporation with sulphuric acid. The methods were compared in the case of a sample of brass, and of phosphor-bronze. The metals were dissolved in nitric acid, and the tin removed by filtration in the usual way. For determination of the lead as sulphate, the filtrate from the tin was evaporated with sulphuric acid, and the precipitate treated in the customary manner. For the estimation of the lead by the "iron-molybdate" method, to the filtrate from the tin was added 0·0500 gram of iron as ferric chloride and then ammonia in excess. The precipitate containing the lead and the iron was treated as described above, and the following results were obtained:

| | Lead by sulphate method. Per cent. | Lead by "iron-molybdate" method. Per cent. |
|---|---|---|
| Brass (containing a little tin) ............ | 0·72 | 0·78 |
| Phosphor-bronze......... .............. ...... | 0 56 | 0·61 |

It will be noticed that the ordinary sulphate method gives results rather lower than those obtained by the "iron-molybdate method." In view of the appreciable solubility of lead sulphate, this was to be expected.

In conclusion, the authors desire to express their thanks to Mr. G. T. Holloway, to whom they are indebted for the alloys on which the above experiments were carried out.

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# CXII.—*The Spontaneous Crystallisation of Solutions of Potassium Chloride, Bromide, and Iodide.*

By Bernard Mouat Jones and Popatlal Govindlal Shah.

In the investigation of the spontaneous crystallisation of solutions of the nitrates of potassium, rubidium, and cæsium, one of the authors had observed (Jones, T., 1908, **93**, 1739) a relation between the extents of the metastable regions in aqueous solutions of these salts having a common anion. The work recorded below was undertaken with a view to determine whether in the case also of similar salts with a common cation any similar relation exists. The salts chosen, namely, potassium chloride, bromide, and iodide, were suitable for the purpose, as they all crystallise in the anhydrous condition and in the cubic system; they are, further, moderately soluble, and the viscosity of their supersaturated solutions should not offer serious hindrance to spontaneous crystallisation.

The work was begun and almost finished before that of Young on the mechanical stimulus to crystallisation (*J. Amer. Chem. Soc.*, 1911, **33**, 148) had come to our notice. Young's work affords strong evidence that no "metastable limit" exists; its apparent existence depends on the fact that in the experiments of Miers, Hartley, Jones, and others to determine the supersolubility curves of various solutions, the amount of mechanical stimulus afforded by shaking the solutions with hard substances (glass or garnet) has coincided with a "transitional" value. By plotting the temperatures of crystallisation against the energies of the shocks employed to induce crystallisation in water, benzene, and fused hydrated calcium chloride, curves of a hyperbolic character were obtained, which indicated that during a certain small range of temperature—the "transitional" region—shocks of considerably varying intensity would bring about crystallisation. Above this region the curve is asymptotic to the energy axis, indicating that a very large additional shock is necessary to raise the temperature of crystallisation by a small amount; below, the curve is asymptotic to the temperature axis, indicating that the supercooled liquid or solution is in a state very sensitive to shock, in which crystallisation is brought about by very small stimuli. The supersolubility curves are explained by Young as corresponding with these "transitional" regions; and so far as it goes the explanation appears to accord well with the facts. It is interesting that the "transitional" region found by Young for pure water lies in the neighbourhood of −0·6°, the value obtained for the point of spontaneous crystallisation of ice by the shaking method.

Young's explanation of the supersolubility curves cannot, however, be considered complete, for although the intensity of the stimulus applied may be a large, perhaps the main, factor in bringing about crystallisation, it is likely that other, as yet undetermined, influences are at work, perhaps those of the nature suggested by Hartley and Thomas (T., 1906, **89**, 1031). For if the intensity of the shock were the only factor to be considered, it is difficult to understand why in such closely similar salts as the nitrates of potassium, rubidium, and cæsium, the supersolubility curve should be coincident with the solubility curve in the last case, and at an average distance of 4° and 1° in the two others; or, as is shown in the present paper, the corresponding values for the chloride, bromide, and iodide of potassium should be 10°, 12°, and 3°. It would also be a curious coincidence if in all cases investigated by the shaking method, varying in character from Glauber's salt dissolved in water to triphenylmethane dissolved in benzene and comprising "metastable regions" varying in extent from nothing to 35 Centigrade degrees, the investigators should always have chosen just those conditions of mechanical stimulus which correspond with the "transitional" regions of Young. It would be expected that for substances of widely differing character the stimuli necessary to produce crystallisation and corresponding with the "transitional" region should also vary widely. This, indeed, Young has shown to be the case. It might not unreasonably be expected, then, that in some cases at least among those investigated by the shaking method, where the stimuli employed were all of the same order of magnitude, the "transitional" stimulus would have been greater than that actually employed.

Again, assuming that Young's curves, which are based on three points only in every case, represent the real relation between the energy of the stimulus and the temperature of crystallisation, it is seen that the "transitional" region covers a range of temperature of several degrees. It would be expected, then, that the observed temperatures of crystallisation obtained by the shaking method should also vary through this range. This has not been found, the observed temperatures almost always agreeing closely, even over wide ranges of temperature and concentration, within a few tenths of a degree, in spite of the fact that no attempts were made to keep constant the vigour of the shaking. In the present investigation the rapidity and violence of the shaking were purposely varied through a considerable range.

That other than purely mechanical factors enter into the problem is indicated by the fact that if the solubility-temperature coefficient of the salt is positive, the supersolubility curve runs closely parallel to the solubility curve with a tendency to diverge from it at high temperatures and concentrations; whereas if the coefficient is negative ($Na_2SO_4$ or $Na_2CO_3,H_2O$), the supersolubility curve converges towards the solubility curve with increasing temperature, that is, decreasing concentration.

It would appear, then, justifiable to conclude that no specifically "metastable" region exists within which spontaneous crystallisation (that is, without the presence of crystal nuclei) *cannot* take place. At the same time, however, the supersolubility curves do mark a somewhat sudden change in properties in the supercooled liquids or supersaturated solutions. They do not mark a "metastable limit," yet they indicate a remarkably sharp change in conditions from a state (labile) where the tendency is for crystallisation not to occur except under very violent stimuli, to a state (metastable) in which with moderate shaking, whereby the hindering effect of viscosity is probably largely obviated, separation of the solid phase will *invariably* take place within a very short time. Young's explanation of the supersolubility curves does not diminish their practical importance in defining the boundary between these two states, nor does it take into account those factors, other than purely mechanical, which would appear to play some part in the phenomenon. Whether the explanation advanced by Hartley and Thomas account for these other factors cannot as yet be said to be proved. It does at least invoke the aid of the kinetic theory, which in a problem of this nature it would be unwise to ignore completely. The influence of time as a factor in bringing about the "accident of crystallisation" is also doubtless not to be neglected.

In the present investigation on the chloride, bromide, and iodide of potassium, all three salts have given well-defined supersolubility curves under the conditions of experiment, slow cooling and moderate agitation and mechanical shock. The supersolubility curves for both the ice and the salt phases have been traced.

## EXPERIMENTAL.

The method used was the same as that employed in previous investigations (Hartley, Jones, and Hutchinson, T., 1908, **93**, 825; Jones, T., 1908, **93**, 1739; 1909, **95**, 1672). The tubes were shaken by various means: by hand, by an electric-bell shaker, by a mechanical shaker worked by a hot-air motor, or by a highly-geared hand-turned machine. The energy of the shaking was then widely varied, but the manner and vigour of the shaking seemed to have little or no effect on the temperature of crystallisation. The shape and material of the tube also appeared to be without influence on the temperature of crystallisation. The bulbs of the tubes were blown as thin as was consistent with safety to allow of their contents assuming the temperature of the bath as rapidly as possible. The same results were obtained whether ordinary or Jena glass was used, but perhaps the crystallisation phenomena were most definite in tubes of Jena glass with conical bulbs, this shape giving somewhat greater opportunity for mechanical shock during shaking. Mechanical friction or stimulus was promoted by adding small crystals of garnet (about 2 mm. across); this made the phenomenon of crystallisation much more definite than was the case in the absence of solid substances. Fragments of Jena glass were first used, since, being amorphous, they could have no inoculating effect, but they were found to be unsatisfactory, as they broke up on shaking, giving rise to minute fragments, the presence of which hindered the observation of the first appearance of the crystals, which they closely resembled. Since in all cases the solutions had to be cooled well below the saturation point before crystallisation could be induced, it may be supposed that the garnets, too, although crystalline, had but very small, if any, inoculating effect.

The influence of the rate of cooling of the bath on the temperature of crystallisation was investigated. It was found that so long as the rate was kept reasonably slow, not more than 1° in ten minutes, crystallisation always occurred at the same temperature within a few tenths of a degree (compare Jaffé, *Zeitsch. physikal. Chem.*, 1903, **43**, 585). More rapid cooling caused a lowering of the apparent temperature of crystallisation, due probably to the fact that the temperature fall within the bulb lagged somewhat behind that of the surrounding bath. Slower cooling up to about 1° in half an hour or more had no appreciable effect on the temperature of crystallisation. The rate generally employed was about 1° in fifteen minutes.

Every tube before cooling in the bath was heated in boiling water in order to get rid of all possible solid crystal nuclei. The time during which the tube was heated had apparently no influence on the crystallisation temperature so long as it was more than a certain minimum value of about ten to fifteen minutes, which appeared to be the time necessary to dissolve all traces of solid crystals. A tube heated for periods varying from twenty minutes to three hours would give the same crystallisation temperature at every determination.

The observation of Jaffé (*loc. cit.*), that "the temperature at which spontaneous crystallisation appears sinks very slowly and steadily with the number of times a tube is experimented with," was not confirmed in the present work. The contents of the same tube would crystallise at a definite temperature even after repeated observations extending over four months. Jaffé, however, used neither solids to promote friction nor mechanical shaking, and his results are therefore perhaps hardly comparable with ours.

The separation of the salt phase from the solution almost always took place in the same way. One or two very small crystals, often visible only through a pocket lens, would appear, and these after a short time would multiply rapidly either at the same temperature or on cooling through one or two tenths of a degree. The detection of the first appearance of the crystals was often a matter of some difficulty, and sometimes of a little uncertainty, since even the garnets would occasionally give rise to very minute, colourless fragments easily confounded with minute salt crystals. They could be distinguished, however, by watching whether they grew or not on lowering the temperature. "Showers" of crystals were only rarely observed, and these only in the more concentrated solutions.

The influence of the solvent action of the water on the glass upon the temperature of crystallisation was investigated, and found to be very small. Two tubes of similar size and shape were made, one of Jena and the other of ordinary glass. Solutions of potassium chloride were prepared and sealed up in the ordinary way, and the crystallisation points determined immediately. They gave salt crystals at 38·2° and 29·5° respectively. On repeating the experiments four months later, they were found to be 38·2° and 29·9°. Similarly, a tube containing 4·12 parts of chloride to 100 of water gave ice at −3·8° after four months, whilst a freshly prepared tube containing 3·99 parts of chloride gave ice at −3·6°. The effect of the dissolution of the glass was evidently very small.

### *Crystallisation of Potassium Chloride.*

Table I gives the highest temperatures at which potassium chloride crystallised from aqueous solutions of various strengths. The results

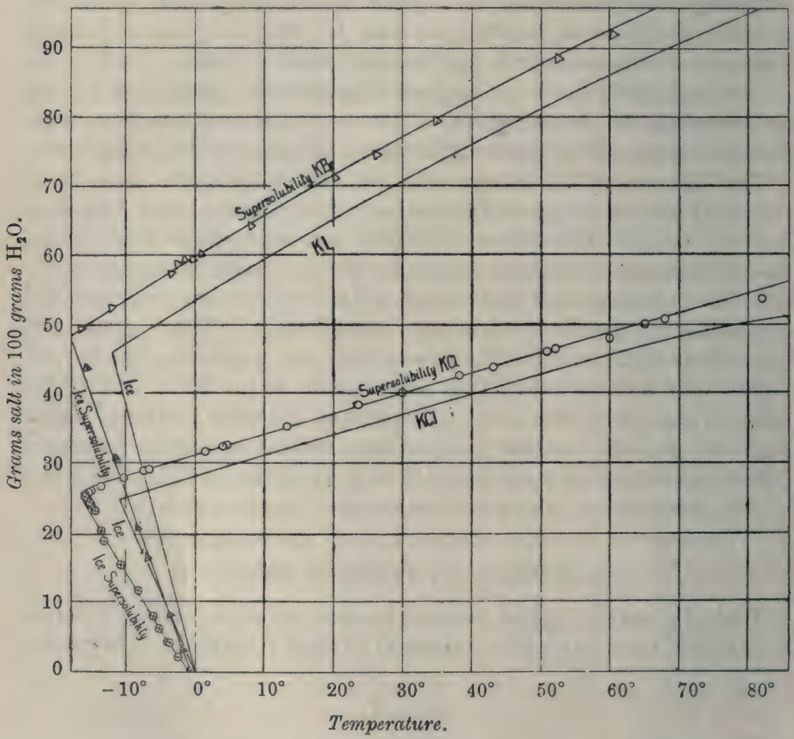
TABLE I.

| Grams of potassium chloride in 100 grams of water. | Temperature of crystallisation of potassium chloride. | Grams of potassium chloride in 100 grams of water. | Temperature of crystallisation of potassium chloride. |
|---|---|---|---|
| 54·09 | 81·9° | 35·55 | 13·3° |
| 51·03 | 67·9 | 32·75 | 4·7 |
| 50·33 | 65·0 | 32·54 | 4·3 |
| 48·32 | 60·0 | 31·84 | 1·2 |
| 46·63 | 52·2 | 29·08 | −6·5 |
| 46·37 | 50·9 | 28·92 | −7·4 |
| 44·02 | 43·2 | 27·93 | −10·2 |
| 44·00 | 43·2 | 26·72 | −13·5 |
| 42·94 | 38·2 | 25·97 | −14·9 |
| 40·32 | 29·9 | 25·87 | −15·2 |
| 38·65 | 23·6 | 25·54 | −15·5 |

are plotted in Fig. 1, which shows both the solubility and supersolubility curves. The phenomenon of crystallisation was very definite, successive determinations often agreeing within one-tenth, and always within three or four tenths, of a degree. The supersolubility curve runs practically parallel to the solubility curve at an average distance from it of 10°.

FIG. 1.

*Solubility and supersolubility curves of potassium chloride and bromide in water.*



○ = *Crystallisation of potassium chloride.*
⊕ = *Crystallisation of ice from dilute solutions of potassium chloride.*
△ = *Crystallisation of potassium bromide.*
⟁ = *Crystallisation of ice from dilute solutions of potassium bromide.*

*Crystallisation of Ice from Solutions of Potassium Chloride.*—Table II shows the temperatures at which ice separates spontaneously from dilute solutions of potassium chloride. The tubes were at first shaken in a freezing mixture contained in a vacuum vessel, which enabled the crystallisation to be observed without removing the tube from the bath, the cooling being brought about by the addition of ice or salt when necessary. It was not, however, easy in this way to secure a regular rate of cooling, nor to maintain the temperature uniform throughout the bath. It was therefore abandoned in favour of a well-stirred toluene bath surrounded by a freezing mixture of ice and salt. The production of the ice phase was quite a definite phenomenon, and the temperatures of crystallisation are seen to lie on a well-defined supersolubility curve (Fig. 1). The ice- and potassium chloride-supersolubility curves give rise to a hypertectic point at about −15·7°. The region in the neighbourhood of the hypertectic point was thoroughly investigated, and a tube containing 25·51 grams of potassium chloride in 100 grams of water gave a mixture of ice and salt crystals at −15·7°.

The temperature at which ordinary pure distilled water crystallised in tubes containing garnets was found to be −0·6°, a value agreeing well with those previously obtained: Hartley, Jones, Hutchinson, −0·5°; Miers, −0·4°; Jones, −0·7°.

TABLE II.

| Grams of potassium chloride in 100 grams of water. | Temperature of crystallisation of ice. | Grams of potassium chloride in 100 grams of water. | Temperature of crystallisation of ice. |
|---|---|---|---|
| 0·00 | −0·6° | 18·77 | −13·0° |
| 2·00 | −2·4 | 20·40 | −13·5 |
| 3·99 | −3·6 | 23·44 | −14·4 |
| 4·12 | −3·8 | 24·09 | −15·1 |
| 6·03 | −5·1 | 24·30 | −15·3 |
| 7·99 | −6·0 | 24·96 | −15·5 |
| 11·73 | −8·1 | 25·19 | −15·7 |
| 15·48 | −10·5 | 25·51 | −15·7 |

*Crystallisation of Potassium Bromide.*

The temperatures of spontaneous crystallisation of solutions of potassium bromide are given in table III, and are plotted in Fig. 1. The character of the phenomena was quite similar to that in the case of the chloride.

The supersolubility curve runs almost exactly parallel to the

TABLE III.

| Grams of potassium bromide in 100 grams of water. | Temperature of crystallisation of potassium bromide. | Grams of potassium bromide in 100 grams of water. | Temperature of crystallisation of potassium bromide. |
|---|---|---|---|
| 112·90 | 107·0° | 64·39 | 8·1° |
| 92·18 | 60·4 | 60·61 | 0·9 |
| 88·78 | 52·6 | 59·89 | −0·1 |
| 79·85 | 34·9 | 59·64 | −1·3 |
| 77·49 | 30·5 | 58·96 | −2·3 |
| 74·97 | 26·2 | 57·37 | −3·5 |
| 71·72 | 20·2 | 52·79 | −11·9 |
| 67·61 | 12·1 | 49·60 | −16·4 |

solubility curve at an average distance from it of about 12°. The data for both the ice and salt solubility curves at temperatures below 0° are contradictory and untrustworthy. In drawing the curves the average values given by Seidell have been adopted.

*Crystallisation of Ice from Solutions of Potassium Bromide.*—Table IV gives the temperatures of spontaneous crystallisation of ice from dilute solutions of the bromide; they are plotted on Fig. 1, where the ice- and salt-supersolubility curves are seen to intersect at the hypertectic temperature of about −18°, the solution then containing about 49 parts of salt to 100 of water.

TABLE IV.

| Grams of potassium bromide in 100 grams of water. | Temperature of crystallisation of ice. | Grams of potassium bromide in 100 grams of water. | Temperature of crystallisation of ice. |
|---|---|---|---|
| 0·00 | −0·6° | 21·00 | −8·2° |
| 3·12 | −1·9 | 31·15 | −11·3 |
| 8·17 | −3·5 | 44·01 | −15·3 |
| 16·49 | −6·8 | | |

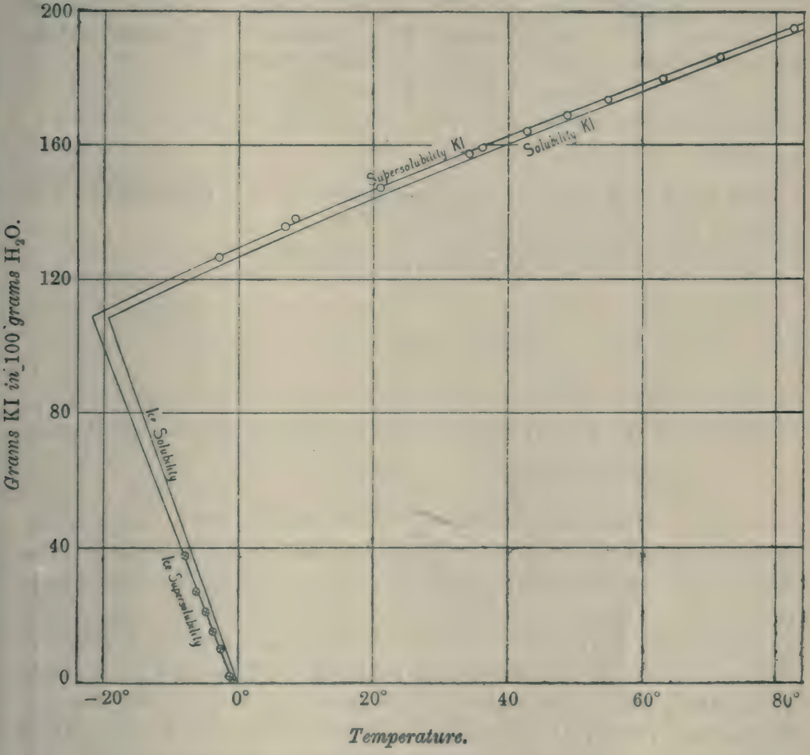
### *Crystallisation of Potassium Iodide.*

In the case of the iodide the "metastable region" appears to be considerably smaller than in the case of the chloride and bromide, namely, about 3° as against 10° and 12°. This made the detection of the first crystals a matter of greater difficulty, since the "relief of supersaturation" on crystallisation was relatively much smaller. Moreover, the crystallisation was a comparatively slow process. The first crystals to appear were only visible through a lens, and always very few in number; they did not themselves grow rapidly, nor as a rule induce rapid crystallisation through the rest of the solution. It was often, in fact, necessary to lower the temperature a few tenths of a degree to make certain that the crystals would grow. Successive determinations of the temperature of first appearance of the crystals, however, gave quite concordant results. For example, tube No. VI (179·6 parts of potassium iodide to 100 parts of water) gave crystals at 63·0°, 63·0°, 63·1° in successive experiments; No. VII (173·7) gave crystals at 54·7°, 55·0°, 55·0°; No. VIII (186·7) gave crystals at 71·8°, 71·7°, 71·7°; No. XIII (141·7) crystallised between 14·2° and 15·3° (preliminary determination), at 14·5° (not at 14·9°), at 14·6° (not at 14·8°). All the tubes showed after heating that hydrolysis had taken place by the brown colour of the liberated iodine; and this was the more noticeable in the more highly concentrated solutions. The amount of chemical action was, however, probably not sufficient materially to affect the temperature of crystallisation.

The results are given in table V and plotted in Fig. 2, where the supersolubility curve is seen to be nearly parallel to the solubility curve. As in the case of the bromide, the ice- and salt-solubility curves given in the figure are based on rather discordant data.

FIG. 2.

*Solubility and supersolubility curves of potassium iodide in water.*



○ = *Crystallisation of potassium iodide.*
⊕ = *Crystallisation of ice from dilute solutions of potassium iodide.*

TABLE V.

| Grams of potassium iodide in 100 grams of water. | Temperature of crystallisation of potassium iodide. | Grams of potassium iodide in 100 grams of water. | Temperature of crystallisation of potassium iodide. |
|---|---|---|---|
| 195·3 | 82·7° | 157·7 | 34·2° |
| 186·7 | 71·7 | 147·2 | 21·1 |
| 179·6 | 63·1 | 145·9 | 19·5 |
| 173·7 | 55·0 | 141·7 | 14·6 |
| 169·2 | 48·9 | 138·0 | 9·4 |
| 164·3 | 43·0 | 135·7 | 7·0 |
| 159·3 | 36·2 | 126·9 | −2·9 |

*Crystallisation of Ice from Solutions of Potassium Iodide.*—The results are given in table VI, and are plotted in Fig. 2. The ice- and salt-supersolubility curves would seem to meet on prolongation at a hypertectic point of about −22°, the solution at that temperature having a concentration of about 108·5 parts of salt to 100 of water.

TABLE VI.

| Grams of potassium iodide in 100 grams of water. | Temperature of crystallisation of ice. | Grams of potassium iodide in 100 grams of water. | Temperature of crystallisation of ice. |
|---|---|---|---|
| 0·00 | −0·6° | 21·51 | −4·8° |
| 1·94 | −1·3 | 27·20 | −6·3 |
| 10·18 | −2·8 | 37·84 | −7·8 |
| 15·30 | −3·9 | | |

The work was done in the laboratories of the Government and Forman Christian Colleges, Lahore, India.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, S.W.

## CXIII.—*The Chemical Nature of Some Radioactive Disintegration Products. Part II.*

By ALEXANDER FLECK, B.Sc.

SINCE the first part of this paper, describing the chemistry of a number of radioactive disintegration products, was written a short time ago, the subject has become of great theoretical importance, due to the elucidation of the general law governing the position of the radio-elements in the periodic table (A. S. Russell, *Chem. News*, 1913, **107**, 49; G. von Hevesy, *Physikal. Zeitsch.*, 1913, **14**, 49; *Phil. Mag.*, 1913, [vi], **25**, 390; K. Fajans, *Physikal. Zeitsch.*, 1913, **14**, 131; *Ber.*, 1913, **46**, 422; F. Soddy, *Chem. News*, 1913, **107**, 97; *Jahrb. Radioaktiv. Elektronik.*, 1913, **10**, 188). The work described in this paper is a continuation of that previously published, and deals with the chemistry of radium-*A*, thorium-*D*, and actinium-*D*, which were the only three substances of period of average life greater than three minutes the chemistry of which remained unknown. By means of a more powerful actinium preparation it has also been possible to confirm the previous conclusion as to the nature of actinium-*B*.

It was early shown in the work that will be described that thorium-*D* differs from lead in many respects (Fleck, *Chem. News*, 1913, **107**, 95), and this was the position when, from the general theoretical laws referred to, it was predicted (Fajans, Soddy, *loc. cit.*) that the *D* members should be analogous to thallium. This prediction, both with regard to thorium-*D* and actinium-*D*, has been fully realised in the course of the work. Since the publication of the first part of the paper, Metzner (*Ber.*, 1913, **46**, 979) has given details of experimental work, in which he shows that thorium-*D* is inseparable from thallium, and confirms the result (Fleck, T., 1913, **103**, 390) that bismuth and thorium-*C* are non-separable. Prior to the publication of Metzner, Soddy had, in a postscript to his paper, published the result, dealt with in this paper, that thorium-*D* may be quantitatively separated from the other members of the active deposit group by precipitating potassium platinichloride in the solution, thus establishing its analogy to thallium.

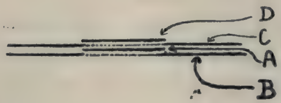
### *Radium*-A.

It was a matter of remark at an early stage in the experimental investigation that polonium remained the only radio-element with chemical properties not possessed by any other. The tables of Fajans and Soddy, however, show that there must be six other substances with chemical properties identical with those of polonium. Of these six, however, radium-*A* is the only one of period sufficiently long to be measured directly, and even in the case of this substance there are numerous difficulties to be overcome which are not met with in the case of the radio-elements previously studied. Only $\alpha$-rays can be used to determine the relative quantities of radium-*A*. $\beta$-Rays, from the radium-*C* produced, cannot be used because, before a deposit of radium-*A* can be dissolved, added to a solution of some substance, and that substance submitted to a chemical reaction and collected, from one to one and a-half minutes must elapse from the instant of withdrawal from the emanation, and in this time about 25 per cent. of the radium-*A* would have changed to radium-*B*. This quantity of radium-*B* would behave, of course, differently from radium-*A*, and what would be finally measured would be, by no means, the initial relative quantities of radium-*A*. It is, of course, impossible to measure relative quantities of a substance giving $\alpha$-rays, like radium-*A*, when distributed through weighable quantities of material owing to the absorption of the rays.

Another difficulty is that no matter how pure initially the radium-*A* may be, its radiation does not decay exponentially to zero, but decays for a number of minutes, after which the activity may remain constant or else rise to a maximum due to the accumulation of radium-*C*, before finally falling to zero with the period approaching that of radium-*B*. The result of this is that all experiments must be made and sufficient measurements taken within about six minutes from the time of withdrawal of the active deposit from the emanation. Otherwise it is impossible to prove that it is actually radium-*A* that is being experimented on.

The first experiments that were made to attempt to confirm the view that radium-*A* and polonium would be identical were concerned with the volatility of these two substances. A copper foil, *A* (see Fig. 1), 4 × 1 cm. in size, was allowed to remain in a hydrochloric acid solution of polonium, some of which was deposited on the copper foil. This foil, after washing and drying, was then laid on a stouter piece of copper foil *B*, of larger area, and with an opening just smaller than 4 × 1 cm. On the top of the foil *A*, a third foil, *C*, rested, which was exactly similar in size to the foil *B*. On the top of the third foil, *C*, a fourth foil, *D*, of the same size as foil *A*, was placed. Foil *A* was then heated for fifteen or twenty seconds with a blow-pipe, which caused the polonium to volatilise and to condense mostly on the top foil *D*. The object in doing this was to get the polonium on a foil in the same physical state for the subsequent volatilisation experiment as the radium-*A* would be, both being deposited from the air. The top foil had a small hole bored in it, so that it could be hooked on to an insulated wire passing through the cork of the flask containng the radium emanation. The wire with the foil attached was then connected with the negative terminal of the 250 volt circuit, and then plunged into the emanation for five seconds. This foil having now radium-*A* on it besides volatilised polonium, took the place of foil *A*, and a fresh foil was placed at *D*, after which the former was heated for a few seconds with a blow-pipe, so that some polonium would be volatilised and some remain. The two foils were then immediately taken to an electroscope with a 0·0031 mm. thick aluminium base, and placed on a stand 3·5 cm. below the base. This distance was calculated so that the intervening air space and the thickness of the aluminium foil absorbed all the α-rays from polonium, whilst the α-rays from the active deposit alone would be measured in the electroscope. One pair of the curves obtained are shown in the accompanying figure (Fig. 2). The top curve, which was obtained from the volatilised substance, shows clearly that when the measurements were started it contained pure radium-*A*, whilst the bottom curve shows that the radium-*A* was not pure, but contains also the radium-*B* and -*C* which have accumulated during the short time that must elapse between removing the foil from the emanation and finishing the volatilisation. From the unvolatilised substance curve it is not possible to deduce any exact measure of the quantity of radium-*A*

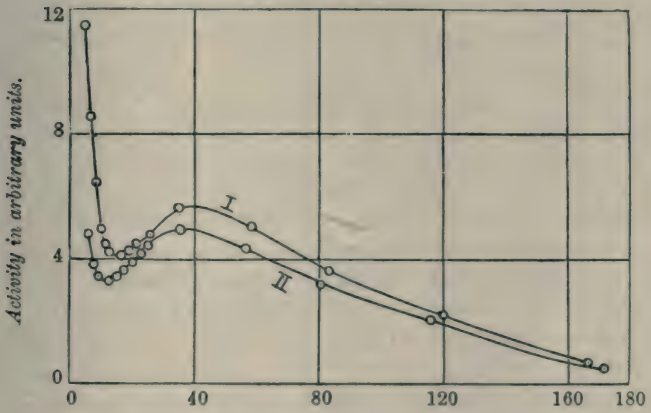
Fig. 1



present, but it can be said that it must be less than the value represented by the curve, since there is a quantity of radium-*C* present. The ratio of the two quantities of radium-*A* must therefore be greater than 2·042—the actual ratio of the activities. The relative quantities of polonium were measured the following day, when it was found that their ratio was 1·161, showing apparently that radium-*A* is more volatile. This difference, however, may not be real, but only apparent. Two elements are said to be non-separable when one cannot be taken away without the other from a uniform mixture of the two. It has to be borne in mind, however, that in this case the polonium is deposited a considerable time before the radium-*A*, and that it may diffuse into the copper foil, from which it will not be so easily volatilised as the radium-*A*. Besides, it may be that we are working with two layers, although they are only of atomic thickness. If that is so it is natural that a greater fraction of the top layer, radium-*A*, would volatilise. It therefore seemed that this experiment should not be regarded as conclusive evidence that radium-*A* was more volatile than polonium.

FIG. 2.

Curve I: *Activity of volatilised substance.*
Curve II: *Activity of unvolatised substance.*



*Time in minutes from separation from emanation.*

The reason for the well-defined maximum, not usually observed, is that the ionisation due to radium-*A* is produced by the last half-centimetre of the range of that $\alpha$-particle, whilst the $\alpha$-particle of radium-*C* has a much longer range, and consequently the ionisation due to radium-*C* is relatively much greater than that due to radium-*A*. That is to say, that in the following equation $\alpha$ has been diminished with reference to $\gamma$ by this experimental disposition. The equation for this curve is:

$$I=K\{ae^{-\lambda_1 t}+be^{-\lambda_2 t}+ce^{-\lambda_3 t}\},$$

where $I$=ionisation, $K$=constant, $t$=time from withdrawal of deposit from emanation, $\lambda_1$, $\lambda_2$, and $\lambda_3$=radioactive constants of radium-*A*, -*B*, and -*C* respectively; and

$$a=(0{\cdot}23\alpha-0{\cdot}0292\beta+0{\cdot}0053\gamma),$$
$$b=(0{\cdot}108\gamma+0{\cdot}0292\beta),$$
$$c=-0{\cdot}114\gamma,$$

where $\alpha$, $\beta$, and $\gamma$ are the numbers of ions produced in the electroscope per atom in the disintegration of radium-*A*, -*B*, and -*C* respectively. Neglecting the number of ions produced by radium-*B*, since that number is very small compared with the numbers from radium-*A* and -*C*, the calculated time, from the instant of withdrawal of the active deposit from the emanation, required to reach the maximum value of the curve is 37·74 minutes. This is in good agreement with the experimental value of approximately 40 minutes.

The only radio-element which could be more volatile than polonium is thorium-*D*, which was known to resemble thallium (see p. 1058). In order to ascertain if radium-*A* was analogous to thorium-*D*, experiments were made with the precipitation of thallium with platinum chloride as platinichloride, and these showed that this precipitate brought down, in a solution of the radium active deposit, radium-*A* in excess of radium-*B* or -*C*. Yet with the complete precipitation of the thallium, only a small fraction—one part in every 14·5 parts of radium-*A*—is thus entrained. Radium-*A* is thus shown to be different from thallium and thorium-*D*.

Recourse was then had to electrolysis. The first attempts were made with the aid of a current from a battery, but finally the natural potential difference between a metal and a solution was used. By simply suspending a copper plate of about 25 sq. cm. area in a hydrochloric acid solution of polonium, and stirring it about in the liquid for one minute, an easily measurable quantity of polonium was deposited. Radium-*A* for all the following experiments was obtained by collecting the active deposit on a strip of magnesium ribbon, 3 cm. long, which was charged negatively on the 250 volt circuit. The ribbon, which was usually immersed in the emanation for about thirty minutes, and had thus a considerable quantity of radium-*B* and -*C* in addition to radium-*A*, was quickly removed from the emanation, dropped into a few c.c. of dilute hydrochloric acid, where it was completely dissolved in from ten to fifteen seconds, and the solution added to the polonium solution. The first experiments showed that, in addition to polonium, radium-*A* containing very little radium-*B* or -*C* was deposited on the copper foil. In this work on radium-*A*, only those metals more electronegative than lead were used. It was not possible to get plates of arsenic, bismuth, or antimony, so that the experiments were confined to copper, silver, gold, and platinum. If lead or a more electropositive metal was used, then the whole active deposit was found on the metal.

The method was then used to see if the same proportion of radium-*A* as of polonium was deposited. This was done by dissolving the active deposit in the usual way in the polonium solution, and then placing simultaneously in the solution for one minute two plates of equal size, one of copper and the other of some other metal. The force driving the polonium and radium-*A* ions on to the copper plate will be different from the force driving them to the other plate, and thus we would expect, if polonium and radium-*A* were dissimilar substances, that, in general, the ratio of the two substances would be different on the two plates, and it might very easily happen that on some metal one was deposited quite readily, whilst the other was not at all deposited. In doing this experiment it is most essential that the two plates be kept electrically insulated from one another. If an electro-couple is formed, as, for instance, if the wires suspending the two plates come in contact with one another, or if one of the plates has an amalgamated surface, then both radium-*B* and -*C* are deposited. The results of the experiment are as follows:

| Metals placed in solution. | Activity due to radium-*A*. | Ratio of activities due to radium-*A*. | Activity due to polonium. | Ratio of activities of polonium. |
|---|---|---|---|---|
| Copper ............... | 5·75 | 2·45 | 39·24 | 2·08 |
| Silver ......... ..... | 2·35 | | 18·89 | |
| Copper ............... | 10·4 | 1·106 ? | 28·54 | 1·132 |
| Gold .................. | 9·4 ? | | 25·19 | |
| Copper ............... | 7·84 | 1·57 | 50·29 | 1·84 |
| Platinum............ | 4·98 | | 27·25 | |

The exact measure of radium-*A* on the gold plate was somewhat difficult to determine, and this is the meaning of the question mark.

The effects obtained are due to radium-*A*, since if the active deposit was dissolved as usual, and allowed to remain twenty minutes until radium-*A* has all disappeared, before a plate was immersed in the solution, only a very small quantity of radium-*B* and -*C* could be detected.

These experiments furnish another proof that radium-*A* is not similar to thorium-*D*. Von Lerch found that thorium-*D* was more difficult to deposit than thorium-*C*. It has been shown that thorium-*C* and radium-*C* have identical electrochemical and chemical properties (von Hevesy, *Phil. Mag.*, 1912, [vi], **23**, 628; Fleck, this vol., p. 393), and that therefore thorium-*D* is more difficult to deposit than radium-*C*. The preceding experiment shows that radium-*A* is much more easily deposited than radium-*C*, and therefore than thorium-*D*. There can be thus no similarity between thorium-*D* and radium-*A*.

The similarity of radium-*A* to polonium was confirmed by showing that, by precipitating a small quantity of bismuth oxychloride in a radium-*A* solution, more than 60 per cent. of the radium-*A* was actually measured on the filter paper, no allowance being made for the absorption of the α-rays. Experiments like this one to ascertain what percentage of radium-*A* was precipitated were made by collecting the active deposit on two strips of magnesium ribbon of exactly the same size, placed in close contact with one another. One piece was then dissolved in acid, and the chemical reaction made, whilst the other was retained as a measure of the initial quantity of radium-*A* present.

Radium-*A* also remains in solution when lead is precipitated from an active deposit solution either as chloride or sulphate. This is shown by the fact that such a precipitate does not show any initial α-ray decay, but, on the contrary, shows a steady increase of α-ray activity.

All these experiments show that radium-*A* and polonium have chemically similar properties.

### *Thorium*-D.

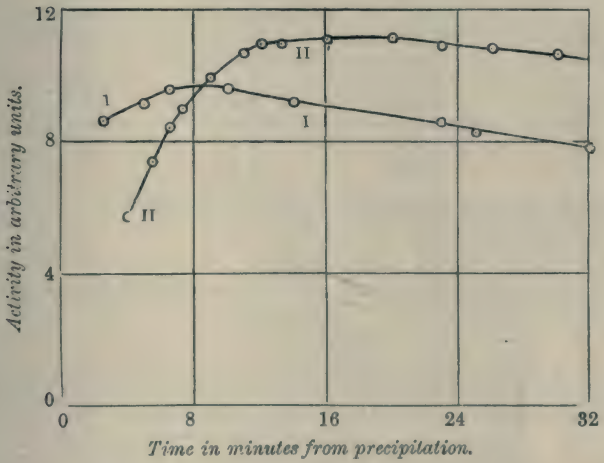
In the initial stages of the work, before anything was known of the chemistry of this substance, the experimental method was to work with pure thorium-*D* obtained by recoil (Hahn, *Ber. Deut. physikal. Ges.*, 1909, **11**, 55). The thorium-*D* was recoiled from a highly polished brass plate, which had been kept negatively charged for twenty-four hours or more over a strongly emanating radiothorium preparation on to a platinum plate. The active material was then dissolved off by dropping the plate into boiling dilute nitric acid. Lead was then added to the solution, which also contained bismuth, and reprecipitated as lead sulphate or lead chloride. By these experiments it was seen that no thorium-*D*, or at most only a small fraction, was precipitated as sulphate or chloride, and hence that it was not analogous to lead.

The fact that all the known elements of atomic weight over 200, with the two exceptions of thallium and mercury, were similar to some of the radio-elements, suggested, even before the tables of Fajans and Soddy had been published, that thorium-*D* would perhaps be similar to one of these elements. Mercury seemed the least likely, and it was soon found experimentally that thorium-*D* was not nearly so volatile as that element.

The experiment was therefore made of adding thallium to a solution of the thorium active deposit in equilibrium, and precipitating the thallium as platinichloride. This precipitate had an activity which decayed to zero with a period of half-value of 3·8 minutes. It was found that the initial γ-activity of the thallium precipitate, measured two minutes after precipitation with platinum chloride, was 54 per cent. of the activity obtained by precipitating the *B* and *C* members immediately after removal of the thallium and allowing the *D* member to come again into equilibrium. It is thus shown that thorium-*D* is precipitated quantitatively with thallium platinichloride. It can also be precipitated completely with potassium platinichloride.

FIG. 3.

Curve I: *β-Ray curve of initially pure thorium*-C.
Curve II: *γ-Ray curve of initially pure thorium*-C.



Other reactions show that thorium-*D* behaves like thallium, and not like potassium. It is precipitated completely by ammonium sulphide from a solution containing potassium, bismuth, thorium-*C*, and thorium-*D*. If the bismuth in such a solution is precipitated either as hydroxide or oxynitrate or as sulphide from an acid solution, the thorium-*D* remains dissolved. This is seen from such curves as are reproduced in Fig. 3. Curve No. 1 is obtained by measuring β-rays from bismuth oxynitrate precipitated from such a solution, and curve No. 2 is obtained by measuring the γ-radiation. It is observed that the β-radiation does not appear to rise from zero to a maximum, whereas the γ-rays have a relatively much smaller initial value. This confirms the recent discovery that thorium-*C* gives β-rays but no γ-rays, whereas thorium-*D* gives both types (E. Marsden and C. G. Darwin, *Proc. Roy. Soc.*, 1912, *A*, **87**, 17; O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1912, **13**, 390).

### *Actinium*-B.

The opportunity was also taken of confirming the view (Fleck, T., 1913, **103**, 394) that actinium-*B* was not only similar to lead, but non-separable from it, by making a series of fractional precipitations of lead sulphate from a solution containing lead and actinium active deposit. Four successive quantities of sulphuric acid gave precipitates Nos. 1, 2, 3, and 4, while the addition of alcohol to the filtrate from No. 4 gave precipitate No. 5.

| Number of precipitate. | Weight of precipitate. Gram. | β-Activity of precipitate 40 mins. from initial precipitation. | β-Activity of precipitate per gram at that time. |
|---|---|---|---|
| 1 | 0·3599 | 7·5 | 20·86 |
| 2 | 0·3732 | 8·1 | 21·66 |
| 3 | 0·1660 | 3·4 | 20·43 |
| 4 | 0·0296 | 0·58 | 19·60 |
| 5 | 0·0169 | 0·35 | 20·70 |

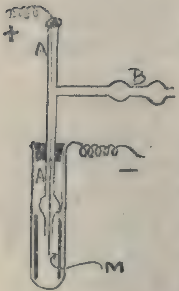
The activities were measured in an electroscope by divisions per minute, and the units are thus arbitrary.

The experiment shows that there is no alteration in the concentration of actinium-*B* in lead by such fractional treatment.

### *Actinium*-D.

From the theoretical considerations already referred to, actinium-*D* should be analogous to thorium-*D* and to thallium. The method of obtaining actinium-*D* in a pure condition was to suspend a needle of which all but a few millimetres were protected by a glass tube, in a tube containing the actinium preparation, and allow it to remain in this position negatively charged to 250 volts for a few hours. The needle was then removed, threaded with copper wire, passed through the tube *AA* (Fig. 4), which was sealed with wax at the top. This tube was then placed in a small glass tube, containing a cylinder *M*, made of sheet magnesium, with which connexion could be made by a fine copper wire. The tube *AA* was then placed in the glass tube and exhausted through the side-tube *B*, whilst the needle was connected with the positive terminal, and the cylinder with the negative ter-

FIG. 4.



minal of the 250 volt circuit. After not less than seven minutes the cylinder was dipped into dilute acid, and the recoiled actinium-*D* thus obtained in solution. Thallium nitrate was added to this solution, and then two successive quantities of hydrochloric acid, and finally ammonium sulphide. The results of this experiment are:

| Number of precipitate. | Weight of thallium present. Gram. | β-Activity of precipitate 5 mins. from start. | β-Activity per gram at that time. |
|---|---|---|---|
| 1 | 0·0900 | 5·0 | 55·6 |
| 2 | 0·0722 | 4·2 | 58·1 |
| 3 | 0·0354 | 2·0 | 56·5 |

Experiments with platinum chloride showed that 88 per cent. of activity due to actinium-*D* obtained by recoil on the magnesium foil could be obtained in a precipitate of potassium platinichloride.

It was also shown that the actinium-*D* was precipitated with the thallium from a solution containing sulphuric acid, oxidised by bromine water to which ammonia was added, a reaction analogous to that employed by Metzner for thorium-*D*. It is also completely precipitated with thallium sulphide by ammonium sulphide and with potassium iodide. It is not precipitated as hydroxide or as sulphide from an acid solution.

These experiments show that actinium-*D* cannot be separated from thallium.

### *Summary.*

It has been shown (1) that radium-*A* and polonium are chemically similar and non-separable; (2) that thorium-*D* is similar to thallium; (3) that actinium-*B* is not only closely allied to lead but non-separable from it; and (4) that actinium-*D* and thallium are two chemically non-separable substances.

These experiments therefore confirm the correctness of the general theoretical law governing the evolution of the radio-elements through the Periodic Table.

I desire to thank Dr. Giesel and the Chinin Fabrik of Brunswick for their kindness in lending a powerful actinium preparation for this research.

I am indebted also to Mr. F. Soddy, F.R.S., for his continued help and advice, and for the use of materials employed in carrying out this research.

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# CXIV.—*The Rotatory Dispersive Power of Organic Compounds. Part I. The Measurement of Rotatory Dispersion.*

### By Thomas Martin Lowry.

About eight years ago experiments were begun with a view to extend the measurement of optical rotatory power to colours other than the yellow sodium light, which at that time was used almost exclusively in chemical laboratories throughout the world. The importance of this extension was obvious. The form of the rotatory-dispersion curves was in most cases not known, but cases of anomalous dispersion had been detected with considerable frequency amongst the substances which had been used most commonly in polarimetric investigations. It was clear that progress was likely to be slow until it was possible to determine the influence of temperature, solvent, concentration, and chemical constitution upon the whole form of the rotatory-dispersion curve, rather than on one single point, which had been selected solely because light of that particular wave-length was cheaply and easily produced.

The aim of the investigation now described was not merely to make observations in the case of a few selected substances, but rather to establish new methods of measuring rotatory dispersion, which should be so simple and easy as to render them generally available for the ordinary routine measurements of the laboratory.

It soon became evident that such standard methods could only be established after an exhaustive study of all the most promising possibilities, and, moreover, that if the methods were to be of permanent utility they must be capable of giving results of the highest order of accuracy, and must therefore be tested with a stringency far exceeding the requirements of present-day routine. It was with this object in view that experiments were begun on the rotatory dispersion of light in quartz (*Phil. Trans.*, 1912, *A*, **212**, 261), since there was no other way in which readings of large magnitude could be taken and then reproduced month after month without any perceptible variation. The labour involved in these experiments has been amply justified by a progressive simplification of methods and of apparatus, which has already brought the measurement of rotatory dispersion within the reach of the advanced student as well as of the original investigator. It is proposed in the following pages to describe these simplified methods of measurement and some of the observations and conclusions to which they have led.

### A.—*Sources of Light.*

In the experiments on quartz it was found that readings which could be reproduced with a variation of only a few parts per million could be taken with light of some 24 wave-lengths in the visible region of the spectrum (*Phil. Trans.*, 1912, *A*, **212**, 288, 289). Many of these were obviously unsuitable for general use, except when a very large number of different wave-lengths are required, for example, to establish the exact form of some anomalous curve. In particular, it was recognised that the spectra of metallic arcs burning between terminals of copper or brass were not likely to be widely used, both because of the relative complexity of the apparatus, and because of the disagreeable flicker which is almost inseparable from such sources of light; but it was not possible to rule out the cadmium lines on this ground, as three of these, namely:

| | | |
|---|---|---|
| The red line............ | wave-length | 6438·4722 |
| The green line......... | ,, | 5085·8240 |
| The blue ,, ......... | ,, | 4799·9107 |

are of unsurpassed spectral purity, and have already been used very largely as principal standards of wave-length. If it were not for the difficulty of producing a powerful cadmium spectrum, these three lines would undoubtedly appear in the forefront in all measurements of rotatory dispersion; even at the present time they cannot safely be set aside, as the enclosed cadmium arc, which is now somewhat of a curiosity, may at any moment become a commercial product capable of being used under ordinary laboratory conditions. In view of these considerations, a large number of measurements were made with a cadmium spectrum produced by burning an arc between poles of a silver-cadmium alloy (*Phil. Mag.*, 1909, [vi], **18**, 320). The silver arc-spectrum, although much easier to produce, was used but little; one of the green lines is a doublet, occupying practically the same position as the green mercury line, whilst the beautiful dark green line does not differ from it sufficiently to justify the trouble of taking a second set of "green" readings except in the case of substances showing anomalous rotatory dispersive power. A similar statement may be made about the green thallium line; a powerful and steady light can now be produced with great ease by vaporising the chloride from a silica bulb in a stream of oxygen and passing it into a flame (P., 1912, **28**, 65); but it is not likely to be used much, except in laboratories where the arc-spectra are not available.

The accumulated experience of several years has proved conclusively that (at least until the enclosed cadmium arc becomes a commercial proposition) no better line can be selected for standard polarimetric measurements than the green mercury line of wavelength 5461. By means of the echelon spectroscope, the line can be resolved into eight components (Stansfield, *Phil. Mag.*, 1909, [vi], **18**, plate XII); but these extend over a range of less than half an Ångström unit, and are distributed very symmetrically about a dominant doublet, so that the line may be regarded for most purposes as a pure monochromat. Its availability as such for polarimetric work is sufficiently proved by the fact that it has given perfectly clean readings (12789·19° and 12789·21°) after passing through half a metre of quartz. It was, indeed, in the testing of quartz that this line was shown to be unique, since in no other case was it possible with certainty to attribute small variations in the readings to causes which were entirely independent of the source of light. The violet line of wave-length 4359 is also of unique value as a source of monochromatic violet light, and as such is likely to remain for many years the second absolutely essential feature in all ordinary measurements of rotatory dispersion. It will be sufficient to point out that where two substances differ in rotatory power by 137 units at wave-length 4359, the dark blue cadmium line of wave-length 4687 gives a difference of only 71 units, whilst the light blue cadmium line of wave-length 4800 gives a difference of only 54 units, the values being assumed to be equal at wave-length 5461. The light blue cadmium line is not easy to read with accuracy even at the present time; the dark blue cadmium line proved to be so difficult and fatiguing that it was soon abandoned as a source of light for routine measurements; the violet mercury line, on the other hand, when derived from a modern commercial mercury arc, is so powerful and steady that it can be read with ease and accuracy, using a half-shadow angle of only 4° to 5°. The presence of two satellites introduces an error which does not exceed 1 part in 10,000, and may therefore be neglected in all readings of less than 100°.

The selection of a suitable line for use at the red end of the spectrum is less easy. The red cadmium line of wave-length 6438 is easier to read than the red zinc line of wave-length 6364; but the red lithium line of wave-length 6708 is the one that has been used most frequently. Even under favourable conditions it can only be read with a half-shadow angle of 7° or 8°, and little reliance can be placed on the second decimal (0·01°) of the readings; but these disadvantages are compensated by its greater wave-length, which serves to magnify considerably the effects of rotatory dispersion.

The first routine-measurements were made with a series of nine lines:

| Li. | Cd. | Na. | Hg. | Hg. | Cd. | Cd. | Cd. | Hg. |
|---|---|---|---|---|---|---|---|---|
| 6708 | 6438 | 5893 | 5790<br>5769 | 5461 | 5085 | 4800 | 4678 | 4359 |
| Red. | | Yellow. | | Green. | | Blue. | | Violet. |

The series was soon reduced to eight by omitting the dark blue cadmium line. This would be one of the most valuable of the series if it could be more easily read, but the strain involved was so excessive that it had to be abandoned. The yellow mercury doublet 5790 and 5769 was also dropped as being redundant, and also because it is so far from being monochromatic that there is little real difficulty in reading the components separately. If a powerful cadmium arc were available, the above series (with the mercury doublet omitted, but the dark blue cadmium line restored) would give an almost ideal list of eight monochromatic lines, which might be relied on to survive the test of many years of actual service. It would include some of the purest and most powerful lines that have been observed amongst the spectra of the elements, and would require a minimum amount of apparatus both for producing the spectra and for resolving them into their constituent lines.

Polarimetric measurements with this series of lines soon revealed the fact that most of the curves belonged to one family, so that agreement at two points usually implied agreement throughout the whole of the rotatory-dispersion curves. Under these conditions, when once the form of any particular curve had been established, attention was concentrated on the careful measurement of a smaller number of lines; the cadmium lines, which still involved the use of a rotating metallic arc, were therefore frequently omitted, thus reducing the series to four lines:

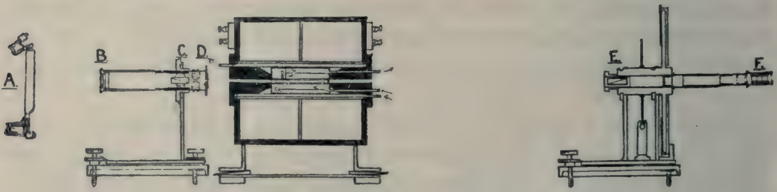
| Li. | Na. | Hg. | Hg. |
|---|---|---|---|
| 6708 | 5893 | 5461 | 4359 |

(Compare Dorn and Lohmann, *Ann. Physik*, 1909, [iv], **29**, 535.)

Finally, when it was discovered that the rotatory-dispersion curves could be expressed by an equation involving only two constants, attention was directed almost exclusively to a very careful reading of the green and violet mercury lines. From these readings the other points on the curve could then be calculated with a degree of accuracy exceeding that which could be attained in any one individual series of observations. The lithium and sodium lines were then no longer an essential part of the scheme of measurements; but it was desirable to retain the red line as a check upon the normal character of the curves, whilst the sodium line was still used sometimes in order to keep directly in touch with earlier observations.

### B.—*Apparatus.*

From the preceding statement it will be seen that in the course of seven or eight years the measurement of rotatory dispersion has been reduced from tedious and fatiguing observations of eight and nine wave-lengths to the rapid and easy observation of two lines only. An equal simplification has been effected in the apparatus used. At first the light was purified by passing through a constant-deviation spectroscope before entering the polarimeter. The presence of stray light rendered necessary the addition of a direct-vision prism on the eye-piece as employed by Perkin (T., 1906, **89**, 615) for a similar purpose. This twofold spectroscopic purification (*Phil. Trans.*, 1912, *A*, **212**, 268) still provides the most luxurious way of reading a polarimeter with lights of various colours, and is essential in all cases in which a complex spectrum has to be resolved, as, for instance, when the cadmium lines are read with the help of a cadmium-silver arc. In the case of the red lithium and the violet mercury line, however, the double resolution necessitates a greater sacrifice of light than is practicable in taking readings at the ends of the visible spectrum; these lines must therefore be read with a direct-vision prism only. It is one of the merits of the scheme of standard wave-lengths discussed in the preceding paragraphs that the four lines specially chosen for routine measurements can all be read with this simplified arrangement. With the help of an enclosed arc, it should also be possible to read the cadmium lines in the same way, thus giving a full series of eight lines without the use of an auxiliary spectroscope.



*Simple apparatus for measuring rotatory dispersion.*

NOTE.—The apparatus is shown as arranged for reading the magnetic rotatory power of a shortened column (100 mm.) of liquid (compare Part III. of this series of papers).

The actual arrangement, as applied to the measurement of magnetic rotatory power, is shown in the diagram, where *A* is a mercury lamp, *B* is a condensing lens, *C* is the triple-field, *D* is a slit, *E* is the analysing prism, *F* is a direct-vision prism attached to the eyepiece. In adapting an ordinary polarimeter for measurements of rotatory dispersion, it is only necessary to add to it the direct-vision prism *F*, and the slit *D*. The latter may be merely two pieces of paper fixed to the glass window which protects the polarising prisms. Apart from the mercury lamp, the cost of the adaptation is therefore insignificant. If a full field is required it is convenient to use an extra dense direct-vision prism to separate the mercury green line from the yellow doublet, but it is still advisable to use a light prism for the violet, as the denser prisms tend to cut off the light.

The apparatus for producing light need not be described in detail. Several mercury lamps specially suited for spectroscopic and polarimetric work have already been described (*Trans. Faraday Soc.*, 1912, **7**, 267; *Proc. Roy. Inst.*, April 18th, 1913; compare *Engineering*, April 24th, 1913). The other methods of illumination are set out in the paper already referred to (*Phil. Trans.*, 1912, *A*, **212**, 269).

Apparatus has also been devised for taking polarimetric readings in the infra-red and ultra-violet regions of the spectrum. This will be described in detail in connexion with experiments on the dispersive power of quartz, of which it formed an essential feature.

The expenses of the experiments described in this series of papers have been defrayed to a very large extent by generous grants from the Government Grant Fund of the Royal Society, for which the author wishes to express his gratitude. He also wishes to thank Mr. W. P. Paddison and Mr. H. R. Courtman for valuable assistance in the experimental work.

## CXV.—*The Rotatory Dispersive Power of Organic Compounds. Part II. The Form of the Rotatory-dispersion Curves.*

By Thomas Martin Lowry and Thomas William Dickson.

Perhaps the most interesting result of the investigations now described has been to disclose the fact that the rotatory-dispersion curves of many organic compounds are of such a simple form that they can be expressed by means of equations containing only two arbitrary constants.

In the case of quartz, the rotatory power in the visible region of the spectrum was expressed by the equation:

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k}{\lambda^2},$$

where $\lambda_1^2 = 0{\cdot}010627$ represents an absorption band in the inaccessible ultra-violet region at wave-length 1030 ($0{\cdot}1030\mu$), $\lambda_2^2 = 78{\cdot}22$ represents a band in the deep infra-red at wave-length

88,440 ($8 \cdot 844\mu$), whilst the third term implies the existence of a band so far out in the ultra-violet that $\lambda_3^2$, the square of its wave-length, is negligible. In order to make the equation express the rotatory power of quartz in the ultra-violet region, it is necessary to give a finite value to $\lambda_3^2$; the equation then includes a third term, $\frac{k_3}{\lambda^2 - \lambda_3^2}$, and involves not less than six constants.

An investigation of the rotatory-dispersive power of a large number of organic compounds has shown that both the optical and the magnetic dispersions can be expressed by the simple equation:

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}.$$

This equation has the merit of separating completely and easily the rotatory power of a substance from its dispersive power, so that these can now be measured and discussed as separate and independent properties.

"*Absolute Rotatory Power.*"—Every substance which obeys this dispersion law may possess a rotatory power ranging from zero to infinity according to the wave-length of the light employed. A casual measurement of its optical rotatory power for one arbitrary wave-length is therefore no guide to its power of rotating the plane of polarisation, and does not afford any real measure of the asymmetry of the molecule. Such a measure is, however, afforded by the constant $k$ of the above equation; this may be described as the "*rotation constant*" of the equation. From the form of the function in which it appears, it is clear that the "rotation constant" $k$ has not the same dimensions as the "rotation" $\alpha$, but must represent the product of a rotation multiplied by the square of a length. But it is at once evident that the numerical value of $k$ will be equal to the numerical value of $\alpha$ when $\lambda^2 - \lambda_0^2 = 1$. This particular value of $\alpha$ (which, but for the difference in dimensions, might be substituted for $k$ in the equation) we propose to describe as the "*absolute rotation,*" representing it by the symbol $\alpha_0$ or $\alpha_{abs}$. The equation might indeed be rewritten as:

$$\frac{\alpha}{\alpha_0} = \frac{[L]^2}{\lambda^2 - \lambda_0^2},$$

where $[L]$ is simply the unit of length.

It should be noted that the term "absolute" is used here to describe the selection of a particular wave-length as a standard in recording the rotatory power of a substance. It may therefore be applied either to the observed rotation, to the specific rotation, or to the molecular rotation, using for this purpose the symbols:

$$\alpha_{abs.} \qquad [\alpha]_{abs.} \qquad [M]_{abs.}$$

In handling the equation, it is convenient to express the wave-lengths in microns, so that the sodium doublet has wave-length $0{\cdot}5893\mu$, whilst the corresponding values for the green and violet mercury lines are $0{\cdot}5461\mu$ and $0{\cdot}4359\mu$. As $\lambda_0^2$ is usually small, at least in the case of colourless substances, the "absolute rotatory power" is the value which would be observed at a wave-length, given by $\lambda^2 = 1 + \lambda_0^2$, not far removed from 1 micron or 10,000 Ångström units. Thus the "absolute rotatory power" of a large number of simple organic compounds for which $\lambda_0^2 = 0{\cdot}02$ (approx.) is substantially identical with the values which would be observed if readings were taken with the infra-red mercury line at wave-length $1{\cdot}0140\mu$ or 10,140 Ångström units; these "absolute rotations" are about 28 per cent. of the values for the green mercury line, and 33 per cent. of the values for the yellow sodium doublet.

"*Dispersive Power.*"—The simplest method of expressing the dispersive power of a substance is to give the ratio $\alpha_{4359}/\alpha_{5461}$ of the readings for the violet and green lines of the mercury spectrum. This may be described as the chief "*dispersion ratio*" of the substance. But with the help of the formula given above there is no difficulty in providing a measure of the dispersion which shall be independent of the particular wave-lengths selected for observation. Such a measure is afforded by the "*dispersion constant*" $\lambda_0^2$ of the equation.

This constant represents the square of the wave-length of the dominant absorption band. If the band were so far removed into the extreme ultra-violet that $\lambda_0^2$ became negligible, the substance would obey Biot's law: $\alpha = k/\lambda^2$, the rotation being inversely proportional to the square of the wave-length. Biot's law appears, indeed, to express the lower limit of dispersive power as it would be observed in an absolutely transparent medium. Such a medium does not appear to exist amongst optically active compounds, and if it did its optical rotatory power would probably be reduced to the vanishing point. In all the actual cases that have been studied the dispersion is increased by the presence of absorption in the ultra-violet region, whereby $\lambda^2$ is converted into $\lambda^2 - \lambda_0^2$. The greater the wave-length $\lambda_0$ of the absorption band, the greater will be the dispersive power of the medium, at least until the band passes over to the infra-red side of the wave-lengths under consideration. This increase of dispersion depends directly on the magnitude of $\lambda_0^2$, which is thus a measure of the dispersive power of the medium as distinct from the dispersion, which seems to be inseparable from the phenomenon of optical rotation in every medium in which it occurs.

It is remarkable that the dispersion ratio $\alpha_{4359}/\alpha_{5461}$ never seems to fall much below $1{\cdot}630$, whether in quartz, in water, in a hydrocarbon, or in simple compounds containing carbon, hydrogen and oxygen, provided that these do not show anomalous rotatory dispersion. In all these substances there seems to be a dominant absorption band between $\lambda_0^2=0{\cdot}01$ and $0{\cdot}02$. It is therefore convenient to take a substance for which $\lambda_0^2=0{\cdot}01$ as possessing unit dispersive power, and to measure the "*dispersive power*" of any other substance by the constant $100\lambda_0^2$. On this scale, the "dispersive power" of the simpler alcohols would be about 2·0 units for magnetic rotations, and 2·8 units for optical rotations, whilst the dispersive power of carbon disulphide (magnetic) would be as high as 4·8 units.

*Exact Form of the Curves.*—In view of the small magnitude of the readings, the formula for the rotatory dispersion in organic compounds could not be tested with the same accuracy as in the case of quartz. These readings were taken to six or seven significant figures, but even then it was not possible to detect the influence of more than one of the two known infra-red bands, nor could the position of the second ultra-violet band be determined even approximately from readings in the visible region of the spectrum. When investigating the simpler organic compounds, it was not easy to take readings which could be relied on to 1 part in 1000; that is, one or two hundredths on a reading of 10° to 20°. It was therefore impossible, in the case of substances of normal dispersive power, to determine whether the dispersion was influenced by more than one "free period" of vibration; such a question could only be answered by increasing the magnitude of the observed rotations and by extending the readings as far as possible into the ultra-violet and infra-red regions of the spectrum.

From the practical point of view, however, it is a distinct advantage that these requirements can be set aside by using a simple formula which expresses the form of the curves beyond the limits of accuracy which are possible in ordinary observations. Even in the case of quartz, if the dispersion ratios are taken out to three places of decimals instead of six, no errors greater than 0·001 are introduced when the figures are calculated with the help of the simple formula now put forward for organic compounds.

*Numerical Data.*—In establishing the form of the rotatory-dispersion curve for the simpler organic compounds, it was impossible to come to any satisfactory conclusion on the basis of a few readings taken with a small number of selected substances. Even in reading the sodium and mercury (violet) lines, it is easy to make an error of, say, 0·02° in the observations and 0·002 in the dispersion ratios, whilst in the case of the lithium and cadmium lines the errors may easily be twice as great. For this reason great importance attaches to the cumulative evidence afforded by the data collected together in table I. Each figure in this table represents an average figure obtained from some 20 to 100 settings of the instrument, so that the number of observations condensed into a single table can scarcely be less than 20,000. The value of this accumulation of data is at once seen in the third panel of the table, which contains data for 17 alcohols, 6 acids, and 2 paraffins. When the dispersion ratios for these 25 substances are averaged, the agreement with the calculated figures is practically perfect, but the individual values are seen to vary by ±0·003 in the case of the yellow sodium and green cadmium readings, by ±0·005 for lithium red, ±0·008 for cadmium red, and ±0·01 for cadmium blue. No significance attaches to variations in the violet to green ratio (which is probably subject to an error of ±0·002), as this was merely used to decide which substances should be included in each of the different panels.

The substances included in the lower panels of the table are not only more dispersive than those in the earlier panels, but also have much higher rotatory powers. Their dispersion ratios are therefore much more accurate, and show an extremely satisfactory agreement with the calculated ratios in spite of the relatively small number of readings which are included in each average.

*Magnetic and Optical Rotatory Dispersion.*—It is not proposed to discuss at this point the validity of Wiedemann's law of the proportionality of optical and magnetic rotatory power throughout the spectrum, but attention may be directed to the proof that is now afforded of the identical form of the two types of dispersion curves. Most of the data in the table are for magnetic rotatory dispersion, but identical formulæ have served for the calculation of optical rotatory dispersion. This is seen most clearly by the identical values, shown in the first panel of the table, for the "optical" and "magnetic" dispersion ratios for quartz. The statement is also true of substances which do not obey Wiedemann's law. In particular, it may be noted that the dispersion ratios for phenylethylcarbinol (opt.), shown in column 6, agree very closely with those for allyl alcohol (mag.), as well as with those calculated from the formula. The magnetic values for this carbinol, on the other hand, are found in column 8, in close agreement with the ratios for the optical and magnetic rotatory dispersions in phenylmethylcarbinol.

*Graphic Representation.*—When the rotatory power of a substance is plotted against the *square* of the wave-length, the dispersion curve (if normal) is a simple rectangular hyperbola running asymptotically to zero rotatory power at infinite wave-length and to infinite

*Form of the Rotatory-dispersion Curve.*

| | | Red. | | Yellow. | Green. | | Blue. | | Violet. |
|---|---|---|---|---|---|---|---|---|---|
| | | Li<br>6708. | Cd<br>6438. | Na<br>5893. | Hg<br>5461. | Cd<br>5086. | Cd<br>4800. | Cd<br>4678. | Hg<br>4359. |
| 1. Quartz (magnetic) | | 0·646 | — | 0·851 | 1·000 | 1·167 | 1·318 | — | 1·627 |
| Quartz (optical) | | 0·648 | 0·706 | 0·851 | 1·000 | 1·164 | 1·319 | 1·394 | 1·627 |
| Calculated $a_0=0·2809$ $\lambda_0^2=0·0173$ | | 0·649 | 0·707 | 0·851 | 1·000 | 1·164 | 1·318 | 1·394 | 1·627 |
| 2. Methyl alcohol (mag.) | $CH_3\cdot OH$ | 0·645 | 0·707 | 0·851 | 1·000 | 1·164 | 1·315 | 1·386 | 1·624 |
| Ethyl ,, ,, | $C_2H_5\cdot OH$ | 0·638 | 0·708 | 0·849 | 1·000 | 1·166 | 1·318 | 1·393 | 1·626 |
| Propyl ,, ,, | $C_3H_7\cdot OH$ | 0·642 | 0·713 | 0·850 | 1·000 | 1·163 | 1·321 | — | 1·629 |
| Average | | 0·642 | 0·709 | 0·850 | 1·000 | 1·164 | 1·318 | 1·390 | 1·626 |
| Calculated $a_0=0·2809$ $\lambda_0^2=0·0173$ | | 0·649 | 0·707 | 0·851 | 1·000 | 1·164 | 1·318 | 1·393 | 1·626 |
| 3. *iso*Propyl alcohol (mag.) | $CHMe_2\cdot OH$ | 0·642 | 0·702 | 0·850 | 1·000 | 1·163 | 1·320 | — | 1·634 |
| *n*-Butyl ,, ,, | $C_4H_9\cdot OH$ | 0·649 | 0·707 | 0·849 | 1·000 | 1·168 | 1·328 | — | 1·637 |
| *iso*Butyl ,, ,, | $CHMe_2\cdot CH_2\cdot OH$ | 0·648 | 0·699 | 0·846 | 1·000 | 1·162 | 1·321 | — | 1·635 |
| *sec.*-Butyl ,, ,, | $CHMe(OH)\cdot C_2H_5$ | 0·645 | 0·713 | 0·850 | 1·000 | 1·164 | [1·309] | 1·391 | 1·635 |
| *iso*Amyl ,, ,, | $CHMe_2\cdot CH_2\cdot CH_2\cdot OH$ | 0·650 | 0·709 | 0·852 | 1·000 | 1·169 | 1·325 | — | 1·634 |
| *act.*-Amyl ,, ,, | $CHEt(OH)\cdot C_2H_5$ | 0·647 | — | 0·850 | 1·000 | — | — | — | 1·641 |
| *sec.*-Amyl ,, ,, | $CHMe(OH)\cdot C_3H_7$ | 0·651 | — | 0·852 | 1·000 | — | — | — | 1·636 |
| *sec.*-Hexyl ,, ,, | $CHMe(OH)\cdot C_4H_9$ | 0·647 | 0·705 | 0·852 | 1·000 | 1·165 | 1·321 | — | 1·639 |
| *n*-Heptyl ,, ,, | $C_7H_{15}\cdot OH$ | 0·644 | 0·708 | 0·855 | 1·000 | 1·162 | 1·320 | — | 1·635 |
| *sec.*-Heptyl ,, ,, | $CHMe(OH)\cdot C_5H_{11}$ | 0·648 | — | 0·849 | 1·000 | — | — | — | 1·639 |
| *n*-Octyl ,, ,, | $C_8H_{17}\cdot OH$ | 0·647 | 0·705 | 0·851 | 1·000 | 1·166 | 1·320 | — | 1·636 |
| *sec.*-Octyl ,, ,, | $CH_3\cdot CH(OH)\cdot C_6H_{13}$ | 0·642 | 0·705 | 0·849 | 1·000 | 1·163 | 1·320 | 1·394 | 1·635 |
| *sec.*-Nonyl ,, ,, | $CH_3\cdot CH(OH)\cdot C_7H_{15}$ | 0·649 | — | 0·849 | 1·000 | — | — | — | 1·635 |
| ,, ,, ,, | $C_2H_5\cdot CH(OH)\cdot C_6H_{13}$ | 0·644 | 0·703 | 0·853 | 1·000 | 1·165 | 1·322 | — | 1·634 |
| *sec.*-Decyl ,, ,, | $CH_3\cdot CH(OH)\cdot C_8H_{17}$ | 0·642 | — | 0·848 | 1·000 | — | — | — | 1·636 |
| *sec.*-Undecyl ,, ,, | $CH_3\cdot CH(OH)\cdot C_9H_{19}$ | 0·645 | — | 0·848 | 1·000 | — | — | — | 1·638 |
| *sec.*-Dodecyl ,, ,, | $CH_3\cdot CH(OH)\cdot C_{10}H_{21}$ | 0·644 | — | 0·849 | 1·000 | — | — | — | 1·639 |
| Average for 17 alcohols | | 0·646 | 0·706 | 0·850 | 1·000 | 1·165 | 1·322 | — | 1·636 |

*Form of the Rotatory-dispersion Curve* (continued).

| | Red. | | Yellow. | Green. | | Blue. | | Violet. |
|---|---|---|---|---|---|---|---|---|
| | Li<br>6708. | Cd<br>6438. | Na<br>5893. | Hg<br>5461. | Cd<br>5086. | Cd<br>4800. | Cd<br>4678. | Hg<br>4359. |
| Formic acid (mag.) | 0·647 | 0·708 | 0·852 | 1·000 | 1·164 | 1·322 | — | 1·635 |
| Acetic ,, ,, | 0·648 | 0·698 | 0·851 | 1·000 | 1·163 | [1·331] | — | 1·631 |
| Propionic acid (mag.) | 0·648 | 0·711 | 0·856 | 1·000 | 1·165 | 1·320 | — | 1·635 |
| Butyric ,, ,, | 0·645 | — | 0·853 | 1·000 | — | — | — | 1·634 |
| *iso*Butyric ,, ,, | 0·646 | — | 0·849 | 1·000 | — | — | — | 1·633 |
| *iso*Valeric ,, ,, | 0·651 | 0·702 | 0·848 | 1·000 | 1·165 | 1·324 | — | 1·636 |
| Average for 6 acids | 0·648 | 0·705 | 0·851 | 1·000 | 1·164 | 1·322 | — | 1·634 |
| *n*-Hexane (mag.) | 0·647 | 0·710 | 0·851 | 1·000 | 1·168 | 1·318 | — | 1·636 |
| *n*-Octane ,, | 0·650 | 0·706 | 0·850 | 1·000 | 1·168 | 1·325 | — | 1·634 |
| Average for 25 substances | 0·647 | 0·705 | 0·850 | 1·000 | 1·164 | 1·321 | — | 1·636 |
| Calculated $a_0=0·2782$ $\lambda_0^2=0·0200$ | 0·647 | 0·705 | 0·850 | 1·000 | 1·166 | 1·322 | 1·398 | 1·636 |
| 4. Water (mag.) | 0·643 | 0·703 | 0·850 | 1·000 | 1·166 | 1·323 | 1·404 | 1·645 |
| *tert.*-Butyl alcohol (mag.) $CMe_3·OH$ | 0·643 | 0·704 | 0·852 | 1·000 | 1·166 | 1·328 | — | 1·645 |
| *tert.*-Amyl ,, ,, $CMe_2Et·OH$ | 0·651 | 0·703 | 0·852 | 1·000 | 1·165 | 1·325 | — | 1·643 |
| Methyl*iso*butylcarbinol (mag.) $OH·CHMe·CH_2·CHMe_2$ | 0·650 | — | 0·850 | 1·000 | — | — | — | 1·644 |
| Average | 0·647 | 0·703 | 0·851 | 1·000 | 1·166 | 1·325 | — | 1·644 |
| Calculated $a_0=0·2763$ $\lambda_0^2=0·0219$ | 0·645 | 0·704 | 0·849 | 1·000 | 1·167 | 1·325 | 1·403 | 1·644 |

*Form of the Rotatory-dispersion Curve* (continued).

| | Red. | | Yellow. | Green. | | Blue. | | Violet. |
|---|---|---|---|---|---|---|---|---|
| | Li 6708. | Cd 6438. | Na 5893. | Hg 5461. | Cd 5086. | Cd 4800. | Cd 4678. | Hg 4359. |
| 5. *sec*-Amyl alcohol (opt.) $CH_3 \cdot CH(OH) \cdot C_3H_7$ | 0·642 | — | 0·846 | 1·000 | — | — | — | 1·652 |
| *sec.*-Hexyl ,, ,, $CH_3 \cdot CH(OH) \cdot C_4H_9$ | 0·639 | — | 0·847 | 1·000 | 1·169 | 1·331 | — | 1·653 |
| *sec.*-Heptyl ,, ,, $CH_3 \cdot CH(OH) \cdot C_5H_{11}$ | 0·638 | — | 0·847 | 1·000 | — | — | — | 1·648 |
| *sec.*-Octyl ,, ,, $CH_3 \cdot CH(OH) \cdot C_6H_{13}$ | 0·640 | 0·699 | 0·847 | 1·000 | 1·168 | 1·329 | 1·407 | 1·653 |
| *sec.*-Nonyl ,, ,, $CH_3 \cdot CH(OH) \cdot C_7H_{15}$ | 0·637 | — | 0·846 | 1·000 | — | — | — | 1·651 |
| *sec.*-Decyl ,, ,, $CH_3 \cdot CH(OH) \cdot C_8H_{17}$ | 0·641 | — | 0·848 | 1·000 | — | — | — | 1·649 |
| *sec.*-Undecyl ,, ,, $CH_3 \cdot CH(OH) \cdot C_9H_{19}$ | 0·643 | — | 0·850 | 1·000 | — | — | — | 1·651 |
| *sec.*-Dodecyl ,, ,, $CH_3 \cdot CH(OH) \cdot C_{10}H_{21}$ | 0·645 | — | 0·848 | 1·000 | — | — | — | 1·653 |
| Average | 0·641 | | 0·847 | 1·000 | | | | 1·651 |
| Calculated $\alpha_0 = 0·2745$ $\lambda_0^2 = 0·0237$ | 0·644 | 0·702 | 0·848 | 1·000 | 1·168 | 1·329 | 1·406 | 1·651 |
| 6. Allyl alcohol (mag.) $C_3H_5 \cdot OH$ | 0·641 | 0·700 | 0·847 | 1·000 | 1·177 | 1·332 | — | 1·672 |
| Phenylethylcarbinol (opt.) | 0·637 | 0·700 | 0·845 | 1·000 | 1·174 | 1·339 | 1·421 | 1·674 |
| Calculated $\alpha_0 = 0·2688$ $\lambda_0^2 = 0·0293$ | 0·639 | 0·698 | 0·846 | 1·000 | 1·173 | 1·337 | 1·418 | 1·673 |
| 7. *iso*Valeric acid (opt.) | 0·631 | 0·695 | 0·841 | 1·000 | 1·178 | 1·355 | — | 1·710 |
| Calculated $\alpha_0 = 0·2607$ $\lambda_0^2 = 0·0375$ | 0·632 | 0·6915 | 0·842 | 1·000 | 1·179 | 1·352 | — | 1·710 |
| 8. Phenylethylcarbinol (mag.) $C_6H_5 \cdot CH(OH) \cdot C_2H_5$ | 0·634 | 0·689 | 0·835 | 1·000 | 1·181 | 1·362 | 1·451 | 1·731 |
| Phenylmethylcarbinol (opt.) $C_6H_5 \cdot CH(OH) \cdot CH_3$ | 0·629 | 0·687 | 0·839 | 1·000 | 1·184 | 1·361 | — | 1·736 |
| ,, ,, (mag.) | 0·624 | 0·685 | 0·839 | 1·000 | 1·184 | 1·363 | — | 1·739 |
| Average | 0·629 | 0·687 | 0·838 | 1·000 | 1·183 | 1·362 | | 1·735 |
| Calculated $\alpha_0 = 0·2553$ $\lambda_0^2 = 0·0429$ | 0·627 | 0·687 | 0·839 | 1·000 | 1·183 | 1·362 | 1·450 | 1·735 |
| 9. Carbon disulphide (mag.) | 0·624 | 0·686 | 0·836 | 1·000 | 1·190 | 1·376 | 1·464 | 1·764 |
| Calculated $\alpha_0 = 0·2499$ $\lambda_0^2 = 0·0483$ | 0·622 | 0·682 | 0·836 | 1·000 | 1·188 | 1·3725 | 1·465 | 1·764 |

rotatory power at a wave-length $\lambda_0$ corresponding with the natural period of free vibration in the molecule.

A very simple method of testing the form of the dispersion curve is to plot the reciprocals of the rotatory powers (or of the dispersion ratios) against the squares of the wave-lengths, using for this purpose the following data:

| Li 6708 | Cd 6438 | Na 5893 | Hg 5461 | Cd 5086 | Cd 4800 | Cd 4678 | Hg 4359 |
|---|---|---|---|---|---|---|---|
| $\lambda^2$=0·45 | 0·4145 | 0·3473 | 0·2982 | 0·2587 | 0·2304 | 0·2189 | 0·1900 |

If the simple dispersion formula is valid, the observations will then plot out to a straight line. An accurate straight line would only be obtained if the dispersion obeyed the simple law: $\alpha = k/(\lambda^2 - \lambda_0^2)$. If two terms were required to express the dispersion, as in the case of ethyl tartrate and other "anomalous" substances, thus:

$$\alpha = k_0/(\lambda^2 - \lambda_0^2) \pm k/(\lambda^2 - \lambda_1^2),$$

the reciprocals would no longer plot out to a straight line. The accuracy of the observations would not, however, usually be sufficient to detect the presence of a second term of similar sign unless there were a considerable difference in the magnitude of the two "dispersion-constants."

### *Summary and Conclusions.*

(1) The rotatory dispersion of a large number of simple organic compounds may be expressed by the formula:

$$\alpha = k/(\lambda^2 - \lambda_0^2),$$

where $k$ is the "rotation constant" and $\lambda_0^2$ is the "dispersion constant" of the substance.

(2) The "rotation constant" $k$ is numerically equal to the "absolute rotatory power," $\alpha_0$, which represents the rotatory power of the substance for a wave-length $\lambda$, such that $\lambda^2 - \lambda_0^2 = 1$. Measuring $\lambda$ in microns, this wave-length is a little greater than 1$\mu$, or 10,000 Ångström units.

(3) The "dispersive power" of a substance is conveniently measured by a unit which is numerically equal to $100\lambda_0^2$. The magnetic dispersive power of the simpler alcohols is about 2·0 of these units, whilst that of carbon disulphide is 4·8 units.

(4) The formula can be applied both to magnetic and to natural rotatory powers.

(5) The rotatory-dispersion curves for normal substances may be plotted out as simple rectangular hyperbolæ against the square of the wave-length, or appear as straight lines if the reciprocals of the rotatory powers are plotted.

# CXVI.—*Perezone.*

### By Frederic George Percy Remfry.

Perezone (pipitzahoic acid) is a crystalline compound occurring in relatively large quantities in the root, "Raiz del Pipitzahuac," of a plant, *Perezia adnata,* found in Mexico. It was first examined by Weld (*Annalen*, 1885, **95**, 188), and has since been the subject of extended investigations by Anschütz and Leather (*Ber.*, 1885, **18**, 709, 715; 1886, **49**, 709) and Mylius (*Ber.*, 1885, **18**, 936), whose more important results may be summarised as follows.

Perezone has the empirical formula $C_{15}H_{20}O_3$, forming salts, $C_{15}H_{19}O_3M$, due to the presence of a phenolic group. It has also the properties of a quinone, in that it (1) possesses a deep orange colour, (2) is readily reduced to a colourless substance, which is quickly reoxidised spontaneously in the air, and (3) yields with aniline and other amines, amino-derivatives, such as anilinoperezone, $C_{15}H_{19}O_3(NHPh)$, which are hydrolysed by boiling with dilute acids, yielding hydroxyperezone, $C_{15}H_{20}O_4$. The latter substance is dehydrated by concentrated sulphuric acid, yielding perezinone, $C_{15}H_{18}O_3$, which has both quinonoid and phenolic properties.

Perezone contains an unsaturated linking, for it yields an unstable dibromide.

Attempts to obtain definite compounds from it by reduction, the action of sulphuric acid, phenylhydrazine, or hydroxylamine, or by distillation with zinc dust, as also an attempt to prepare its ethyl ether, were unsuccessful, but an acetyl derivative, to which reference will be made later, was obtained.

The general behaviour of perezone, and particularly its similarity to hydroxythymoquinone, led Anschütz to suggest that it is a hydroxybenzoquinone, containing not more than two substituent alkyl groups, of which one is unsaturated, and he proposed the following embryonic constitutional formulæ:

$$C_6H_2\left\{\begin{array}{ll}(1) & O\\ (4) & O\\ (2) & OH\\ (x) & C_9H_{17}\end{array}\right. \qquad \text{or} \qquad C_6H\left\{\begin{array}{ll}(1) & O\\ (4) & O\\ (2) & OH\\ (x) & Cn_1H(2n_1+1)\\ (y) & Cn_2H(2n_2-1)\end{array}\right.$$

$$\text{where } n_1+n_2=9.$$

No further investigations of this acid appear to have been carried out until 1906, when Sanders (P., **22**, 134) briefly recorded the results of a number of experiments with it. Sanders rejects the established formula, and proposes in its place $C_{10}H_{14}O_2$, but the reasons for this change are not given. He also states that "by prolonged heating above its melting point it loses carbon monoxide and carbon dioxide, giving at first a lemon-yellow sublimate, which melts at 88—89°, and finally a beautifully crystalline, colourless sublimate, which is insoluble in water, but soluble in most organic solvents. This *compound*, $C_{11}H_{14}O_2$, crystallises from acetone or benzene in glistening prisms, melting at 140°, and having an odour of camphor. Its solutions are optically active, a 2 per cent. solution in alcohol having $[\alpha]_D$ 77·9 at 25°; it does not react with hydroxylamine or aniline, but with acetic anhydride forms a *compound*, $C_{41}H_{50}O_{10}$, which crystallises from acetone in square plates, melting at 114—115°."

He further states that perezone is optically inactive, does not contain methoxy-groups, and yields, on fusion with potassium hydroxide, methylhexylene and butyric acid. He states that perezone seems to behave as a hydroxy-ketone.

Perezone had not been the object of any later communication than Sanders's paper (*loc. cit.*) at the time when this work was carried out, and since it exerts very marked physiological action, having purgative properties for which it is much used in Mexico, it was deemed of interest to examine it carefully in order to contribute further to the knowledge of its constitution. Owing to circumstances, it has not been possible to complete the work, and as it is improbable that the author will again be able to take up this problem, the results so far obtained are given in the hope that they may be of assistance to any future investigator.*

In the first place, it was deemed of importance to establish the empirical formula of perezone by molecular-weight determinations, for Sanders's formula, $C_{10}H_{14}O_2$, appeared to be highly improbable in view of the fact that the salts analysed by Weld and Anschütz and Leather were derived from the formula $C_{15}H_{20}O_3$ by the replacement of one hydrogen atom by a monobasic metal. This was accordingly carried out both by the cryoscopic and ebullioscopic methods, and gave results in agreement with the formula $C_{15}H_{20}O_3$. An ultimate analysis confirmed this formula. Sanders's formula for perezone is therefore incorrect.

It next seemed of interest to reinvestigate Sanders's colourless sublimate, $C_{11}H_{14}O_2$, melting at 140°, and the compound, $C_{41}H_{50}O_{10}$, melting at 114—115°, which he obtained by the action of acetic anhydride on this sublimate. The action of heat on perezone was therefore studied, and it was found that when this compound is heated to 210° an exothermic reaction takes place, the temperature rising to about 270°, and carbon dioxide, water vapour, and an inflammable gas being evolved. The residue, which forms a reddish-black varnish when dissolved in a little alcohol or ether, deposits the compound melting at 140—141° (corr.) in well-formed crystals. This compound may also be obtained by sublimation, or by quick distillation of perezone under normal pressure. When pure it is perfectly colourless, and magnificently crystalline. It contains a phenolic hydroxyl group, and may conveniently be designated pipitzol. Analyses and molecular-weight determinations show that it has the formula $C_{15}H_{20}O_3$, and is therefore isomeric with perezone. It is optically active, as stated by Sanders, but his figure $[\alpha]_D$ 77·9° was not confirmed, the constant value $+13{\cdot}1°$ being obtained for the pure substance. It does not react with aniline, hydroxylamine, or phenylhydrazine, and does not decolorise bromine in chloroform solution. When treated with an ethereal solution of magnesium methyl iodide, it gave a compound, $C_{15}H_{24}O_3$, melting at 145°, which may be termed *tetrahydropipitzol.*

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* After the present work had been written up and shortly before its communication (P., 1913, **29**, 72), Fichter, Jetzer, and Leepin published an investigation (*Annalen*, 1913, **395**, 15) of the properties of hydroxyperezone from the results of which they deduced the constitution of this substance, and of perezone itself. This work covers entirely different ground from the present paper, and is discussed in an addendum.

Pipitzol is readily acetylated by means of acetic anhydride, yielding a monoacetyl derivative, *acetylpipitzol*, $C_{15}H_{19}O_3{\cdot}CO{\cdot}CH_3$, melting at 114—115° (corr.). This is obviously identical with Sanders's compound, $C_{41}H_{50}O_{10}$, of the same melting point. Acetylpipitzol is also identical with the product obtained by Anschütz and Leather (*loc. cit.*) by the action of acetic anhydride on perezone under pressure at 100°.

When acetylpipitzol is hydrolysed by means of acid, pipitzol is regenerated, but when sodium hydroxide is used, the product is an oil which could not be caused to crystallise.

It is shown that pipitzol is identical with the colourless, crystalline compound, melting at 141°, which Anschütz and Leather obtained by the action of ethyl bromide on the silver salt of perezone in an endeavour to form the ethyl ester.

One of the three oxygen atoms in pipitzol is phenolic, the other two appear to be neither hydroxylic, since the compound yields only a monoacetyl derivative, nor quinonoid, since it is colourless, nor ketonic, since it does not react with hydroxylamine, phenylhydrazine, or (in so far as the oxygen atoms are concerned) with magnesium methyl iodide. No definite products were obtained by the oxidation of pipitzol.

Further evidence that perezone is a quinone has been obtained by the action of magnesium alkyl iodides, when *alkylquinoles* of this compound were produced.

By-products produced in the preparation of hydroxyperezone and perezinone have also been studied, and, in conclusion, a number of unsuccessful miscellaneous experiments designed to prepare from perezone compounds likely to assist in the elucidation of its constitution are briefly recorded.

## EXPERIMENTAL.

### *Perezone.*

The compound used for this investigation was in the form of orange-golden leaflets, which softened at 102° and melted at 103—105° (corr.). Further crystallisation from water or alcohol did not alter the melting point.

The figures obtained on analysis were in accordance with those of previous investigators. (Found, C=72·7; H=8·0. $C_{15}H_{20}O_3$ requires C=72·6; H=8·0 per cent.)

Determinations of the molecular weight were carried out by the cryoscopic method in benzene solution:

0·2834 in 14·8 gave $\Delta t$ −0·403°, whence M.W.=238.
0·2629 „ 14·82 „ $\Delta t$ −0·352°, whence M.W.=252.
$C_{15}H_{20}O_3$ requires M.W.=248.

### *Pipitzol*, $C_{15}H_{20}O_3$.

This substance is produced in yields varying usually between 25 and 50 per cent. when perezone is heated under different conditions.

When 1 gram of perezone is melted in a small test-tube containing a thermometer, and slowly heated, evident reaction ensues when the temperature reaches 200—210°, for after the source of heat is removed the temperature rises to about 270°, whilst the liquid darkens in colour, and appears to boil owing to the escape of a mixture of carbon dioxide, an inflammable gas, and water vapour. When the product is cooled and dissolved in a little ether or alcohol, pipitzol crystallises out.

Pipitzol may also be prepared by the quick distillation of perezone; only a small proportion of the substance distils over at a very high temperature as a very viscous, somewhat coloured oil, which crystallises when treated with solvents, the residue in the distillation flask forming a dark amorphous mass.

It may also be prepared by sublimation, as stated by Sanders (*loc. cit.*).

Ten grams of perezone were heated in a glass dish, into which there was fitted a filter funnel, through the neck of which a thermometer was placed, for one and a-half to two hours at 160—170°. Large fern-shaped crystals formed on the sides of the dish and funnel, and were always more or less coloured, since some of the perezone sublimed unchanged. The crystals were collected, washed with a little cold light petroleum, and recrystallised, first from this solvent, then from alcohol, when pure pipitzol was obtained.

No individual substance corresponding with Sanders's yellow sublimate, melting at 88—89°, was observed, but a part of the sublimed substance which melted at about that temperature was found to be a mixture of perezone and pipitzol. The dark residue left in the dish after the sublimation gave a further quantity of pipitzol when subjected to a distillation with steam.

*Pipitzol* crystallises from alcohol in large, colourless plates, which melt at 140—141° (corr.):

0·1013 gave 0·2706 $CO_2$ and 0·0738 $H_2O$. C=72·8; H=8·1.

$C_{15}H_{20}O_3$ requires C=72·6; H=8·0 per cent.

A determination of the molecular weight by the cryoscopic method in benzene gave the following result:

0·2727 in 15·65 gave $\Delta t$ −0·358, whence M.W.=244.

$C_{15}H_{20}O_3$ requires M.W.=248.

The specific rotation was determined in chloroform solution, with the following result:

$\alpha_D$ +1·25°; $c$=4·770; $l$=2-dcm.; $[\alpha]_D$ +13·1°.

This rotation was not altered by further crystallisation of pipitzol from alcohol. In view of the figures given by Sanders, 77·9° for a 2 per cent. solution in alcohol, the rotation of the pure compound was determined under these conditions, when the result was found to agree with that obtained in chloroform solution:

$\alpha_D$ +0·58°; $c$=2·169; $l$=2-dcm.; $[\alpha]_D$ +13·4°.

Pipitzol is slowly volatile with steam. It is fairly readily soluble in cold alcohol, ether, benzene, or acetone, readily so in cold ethyl acetate, or chloroform, and very readily soluble in these solvents when hot. It is sparingly soluble in cold, but fairly readily so in hot, light petroleum. It is insoluble in cold water or aqueous sodium carbonate, but is readily soluble in aqueous sodium hydroxide, yielding a colourless solution, from which it is precipitated unchanged on the addition of acids or on saturating with carbonic acid. A dilute alcoholic solution gives, with a drop of ferric chloride solution, a violet coloration, changing to greenish-black. It does not decolorise bromine in chloroform solution, and does not react with aniline, hydroxylamine, or phenylhydrazine.

### *Acetylpipitzol*, $C_{15}H_{19}O_3{\cdot}CO{\cdot}CH_3$.

Acetylpipitzol is readily prepared in almost quantitative yield by boiling pipitzol with acetic anhydride and sodium acetate. The product is poured into water, and basified with sodium carbonate, when acetylpipitzol separates as a crystalline powder. It is washed with water, and recrystallised from light petroleum.

Acetylpipitzol crystallises from light petroleum in large, colourless prisms, which melt at 114—115° (corr.):

0·1546 gave 0·3990 $CO_2$ and 0·1064 $H_2O$. C=70·4; H=7·6.
$C_{17}H_{22}O_4$ requires C=70·3; H=7·6 per cent.

The molecular weight was determined by the cryoscopic method in benzene solution:

0·1582 in 15·18 gave $\Delta t$ −0·177°, whence M.W.=274.
$C_{17}H_{22}O_4$ requires M.W.=290.

The number of acetyl groups was determined by A. G. Perkin's method (T., 1905, **87**, 109):

0·4779 gave 0·0954 $C_2H_4O_2$. $C_2H_4O_2$=20·0.
$C_{17}H_{22}O_4$ requires for one acetyl group $C_2H_4O_2$=20·7 per cent.

From the mother liquors of the acid hydrolysis carried out in this manner, pure pipitzol was recovered in practically quantitative yield. The specific rotatory power of acetylpipitzol was determined in chloroform solution:

$\alpha_D$ 0·96°; $c=7·782$; $l=2$-dcm.; $[\alpha]_D$ +6·2°.

Acetylpipitzol is insoluble in water, or aqueous sodium hydroxide, and gives no colour with ferric chloride, from which it is clear that pipitzol contains only one phenolic hydroxyl group. Acetylpipitzol is readily soluble in the usual organic solvents, with the exception of light petroleum.

### *Benzoylpipitzol*, $C_{15}H_{19}O_3 \cdot COPh$.

This compound was prepared by the Schotten-Baumann method. It forms colourless prisms from light petroleum, melting at 154—155° (corr.):

0·1508 gave 0·4131 $CO_2$ and 0·0952 $H_2O$. C=74·7; H=7·0.
$C_{22}H_{24}O_4$ requires C=75·0; H=6·8 per cent.

### *Identity of Acetylpipitzol with Anschütz and Leather's Product of Acetic Anhydride on Perezone.*

Anschütz and Leather (*loc. cit.*) attempted to prepare an acetyl derivative of perezone by heating the acid in a sealed tube with acetic anhydride for three days at 100°. In this way they obtained a colourless, crystalline product, melting at 115°, from which, however, they were unable to regenerate perezone by the action of potassium hydroxide. This fact, coupled with the circumstance that the compound was colourless—although an acetyl derivative of a hydroxyquinone should be coloured—caused them to doubt that they had obtained a true acetyl derivative of perezone, in spite of the fact that analyses of the compound agreed well for monoacetylperezone.

A quantity of the above substance was prepared by the method given by these authors, and was obtained in colourless plates and prisms from light petroleum, which melted at 114—115° (corr.). It was insoluble in alkalis, and gave no colour with ferric chloride or Millon's reagent for phenols, and was therefore completely acetylated. The melting point was identical with that of acetylpipitzol, and a mixture of the two melted at the same temperature as the two substances separately. Their properties are similar, and the figures given on analysis agree with those required by the formula $C_{15}H_{19}O_3 \cdot CO \cdot CH_3$. A determination of the acetyl groups showed that only one was present, as with acetylpipitzol, and the product of hydrolysis left in the liquors proved identical with pipitzol, melting at 140°, and not depressing the melting point of the latter. An analysis of the hydrolytic product also gave results agreeing with those required from pipitzol. (Found, C=72·3; H=8·3. $C_{15}H_{20}O_3$ requires C=72·6; H=8·0 per cent.)

Thus the effect of acetic anhydride under pressure on perezone is primarily the same as that of heat, apparently bringing about some rearrangement of the atoms within the molecule. Attempts have been made by the present author to obtain a true acetyl derivative of perezone by heating with acetic anhydride and fused sodium acetate and acetyl chloride under ordinary pressure, but without result, no change apparently taking place.

### *Identity of Pipitzol with Anschütz and Leather's Product of the Action of Ethyl Bromide on the Silver Derivative of Perezone.*

Anschütz and Leather (*loc. cit.*) also attempted to make the ethyl ether of perezone by heating the silver compound under pressure for one hour at 100° with ethyl bromide, and succeeded in obtaining a very small amount of a colourless, crystalline substance, melting at 141°. As the compound was without colour, they expressed great doubt that it was the required ether, and the amount obtained being insufficient for an analysis or any characterisation, they were unable to examine its properties in any way. The fact that this substance was colourless and melted at 141° at once suggested that it might be identical with pipitzol, which has already been shown to be formed by the effect of heat on perezone. Accordingly, 2·5 grams of the silver salt were heated in a sealed tube for an hour at 100° with 12 grams of ethyl bromide, and after filtering from the silver bromide, a good yield of a colourless, crystalline substance was easily obtained. This was washed with cold light petroleum and crystallised from the same solvent, when it was obtained in colourless prisms, melting at 140°. A mixture with pipitzol melted at the same temperature, and the two specimens possessed identical properties, such as solubility in potassium hydroxide, insolubility in sodium carbonate, violet colour turning to green with ferric chloride, etc. There was therefore no doubt that the compound obtained by Anschütz and Leather was really pipitzol. The effect of the higher pressure employed is very noticeable in the time taken to produce the change, three days' heating being required to remove the last traces of perezone when acetic anhydride is used.

### *Action of Magnesium Methyl Iodide on Pipitzol.*

The action of magnesium methyl iodide on pipitzol in ethereal solution gave rise to a substance crystallising from dilute alcohol in colourless, prismatic needles, which melted at 145°. A mixture with pipitzol melted at about 115°:

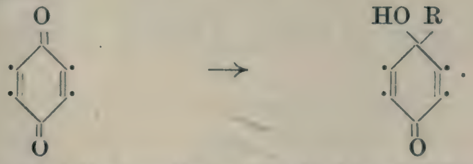
0·0626 gave 0·1640 $CO_2$ and 0·0530 $H_2O$. C = 71·4; H = 9·4.

$C_{15}H_{24}O_3$ requires C = 71·4; H = 9·5 per cent.

This substance, *tetrahydropipitzol*, retains the phenolic character of phenol, gives a bright green colour with ferric chloride, and does not decolorise bromine.

### *Action of Magnesium Alkyl Iodides on Perezone.*

It has been shown by Bamberger (*Ber.*, 1903, **36**, 1625) that when quinones of the benzoquinone type are subjected to the action of magnesium methyl iodide in ethereal solution, the reaction proceeds in part as follows:



Other products of the reaction are quinols and different phenols. In the case of *p*-benzoquinone itself, no additive product was formed, and the author has found that quinol is almost the sole product of the reaction, and is formed in good yield. In order to add further evidence for the quinonoid structure of perezone, it was decided to try the action of magnesium alkyl haloids on it, and the results obtained prove that products similar to those observed by Bamberger were formed.

In the following experiments three molecules of magnesium alkyl iodide were used for each molecule of perezone. A vigorous reaction took place on dropping in the ethereal solution of the acid, and a black mass separated out. The reaction mixture was poured into ice water, and the violet-coloured solution acidified with acetic acid, extracted with ether, and the ether well washed with water.

*Methylquinole of Perezone.*—Clusters of fine, colourless needles from xylene, melting at 111—112°:

0·1497 gave 0·3982 $CO_2$ and 0·1234 $H_2O$. C = 72·5; H = 9·1.

$C_{16}H_{24}O_3$ requires C = 72·7; H = 9·1 per cent.

*Ethylquinole of Perezone.*—Clusters of colourless needles from a mixture of benzene and light petroleum. Melting point 101—102°:

0·0801 gave 0·2143 $CO_2$ and 0·0670 $H_2O$. C = 73·0; H = 9·0.

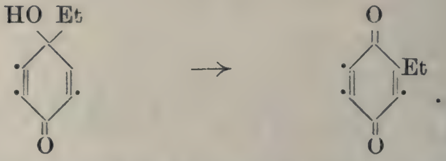
$C_{17}H_{26}O_3$ requires C = 73·4; H = 9·3 per cent.

*Propylquinole of Perezone.*—A clear amber oil, which could not be obtained crystalline; it boils undecomposed at 245—250°/30 mm.:

0·1087 gave 0·2976 $CO_2$ and 0·0926 $H_2O$. C = 74·5; H = 9·4.

$C_{18}H_{28}O_3$ requires C = 74·0; H = 9·6 per cent.

The general properties of the three compounds are the same, and can be described together. They are readily soluble in dilute alkali hydroxides, at first without colour, but the solution quickly becomes brown, and then violet, a characteristic colour reaction given by this class of substances (Bamberger, *Ber.*, 1900, **33**, 3653). They are colourless, and therefore have not the true quinone formula, and are readily oxidised by ferric chloride, giving a quinone-like odour and a bright yellow-coloured compound. In the case of the ethyl compound, a crystalline substance was isolated, which melted at 96—97°, but not in sufficient quantity for analysis. It gave a purple colour with sodium hydroxide similar to that given by perezone, was easily reduced by zinc dust and acetic acid in the cold, and was oxidised again on keeping in the air. This oxidation product was doubtless formed as follows (compare Bamberger, *loc. cit.*):



When warmed with Millon's reagent, these quinole compounds give a yellow coloration indicating a dihydric phenol—a very useful reaction even when the substance is coloured as are perezone derivatives (Mylius, *Ber.*, 1885, **18**, 946).

### *Hydroxyperezone and its By-products.*

In the preparation of hydroxyperezone, $C_{15}H_{20}O_4$, by the action of sulphuric acid on anilinoperezone, both Anschütz and Leather and Mylius noticed the formation of substances which rendered the purification of the main product somewhat difficult.

The melting point of hydroxyperezone is given as 134° by Mylius, and 138° by Anschütz and Leather, but both gave analyses at least 0·5 per cent. too low in carbon content. Hydroxyperezone has now been obtained in a pure state. It melts at 138—139° (corr.), and gives the correct figures on analysis (Found, C = 68·2; H = 7·4. $C_{15}H_{20}O_4$ requires C = 68·2; H = 7·6 per cent.). Two by-products have been isolated in the course of its preparation; one is a *substance*, $C_{15}H_{16}O_4$, melting at 166—167° (corr.), the other a *substance* which does not melt at 300°, and of which the empirical formula has not been adduced with certainty.

Mylius obtained a compound, melting at 165—168°, as a by-product in the preparation of hydroxyperezone, but it contained chlorine owing to the use of hydrochloric acid in the reaction, and is therefore not identical with the substance mentioned above.

The by-product of hydroxyperezone which does not melt at 300° appears to be identical with an impurity of this substance encountered by Anschütz and Leather in quantities too small to permit of analysis or characterisation. They state only that it did not melt, but decomposed at a high temperature, was fairly readily soluble in alcohol or acetic acid, but almost insoluble in ether or benzene.

### *Substance*, $C_{15}H_{16}O_4$, m. p. 166—167° (corr.).

This compound was once obtained when some hydroxyperezone, prepared in the usual way, was dissolved in xylene and set aside in a corked vessel for several months. It was, however, always found in moderate quantities when preparing perezinone, $C_{15}H_{18}O_3$ (Mylius, *loc. cit.*, p. 944), and was isolated as follows. Concentrated sulphuric acid was poured on to hydroxyperezone, and the mixture warmed to 60—70° for five minutes, the liquor was cooled, and water cautiously added, keeping the temperature of the solution below 40°, until a slight, permanent cloud appeared. After some time a dark green substance crystallised out, and was recrystallised from alcohol with the addition of animal charcoal. A mixture of the above-mentioned substance, which does not melt at 300°, and another compound was obtained in this way, and the latter was separated by means of benzene, and crystallised from this solvent, with the addition of light petroleum, in clusters of orange needles, melting at 166—167° (corr.). On further dilution of the acid mother liquors, perezinone crystallised out, and after recrystallisation was obtained pure, melting at 143—144°. Compound, 166—167° (dried at 100°):

0·1403 gave 0·3565 $CO_2$ and 0·0764 $H_2O$. C = 69·2; H = 6·0.
0·0960 „ 0·2428 $CO_2$ „ 0·0506 $H_2O$. C = 69·0; H = 5·9.
$C_{15}H_{16}O_4$ requires C = 69·2; H = 6·1 per cent.

It is readily soluble in most organic solvents and insoluble in water. It is instantly soluble in dilute sodium hydroxide or sodium carbonate, giving the same violet coloration as perezone (perezinone gives a yellow colour), and is reprecipitated unchanged by acids. An acetic acid solution is quickly rendered colourless by reducing with zinc dust, but is soon oxidised back by contact with the air. These two facts point to the compound being a hydroxyquinone like perezone, and as Millon's reagent gives a deep red colour, only one phenolic hydroxyl group is present in the molecule. Ferric chloride gives a purple-brown colour to an acetone solution. It does not combine with aniline, a fact which indicates that all positions in the ring are already occupied.

Perezinone, $C_{15}H_{18}O_3$, which is formed by loss of water from hydroxyperezone, $C_{15}H_{20}O_4$, does not inself combine with aniline for the same reason, and it is probable that the compound in question is formed from perezinone by replacement of two hydrogen atoms of one of the side-chains by an atom of oxygen, since the ring system in each appears to be identified:

$$\underset{\text{Hydroxyperezone.}}{C_{15}H_{20}O_4} \xrightarrow{-H_2O} \underset{\text{Perezinone.}}{C_{15}H_{18}O_3} \xrightarrow{+O_2} \underset{\text{Substance, m. p. 166—167°.}}{C_{15}H_{16}O_4}$$

When this substance, melting at 166—167°, is boiled for half an hour with an alcoholic solution of aniline, it is entirely converted into the substance which does not melt below 300°, the second by-product in the preparation of hydroxyperezone. This interesting change has not, however, been investigated further.

*Substance which does not melt below* 300°.—This substance was first observed by Anschütz and Leather as an impurity in hydroxyperezone. It may be separated from crude hydroxyperezone by fractional crystallisation from alcohol, in which it is less soluble than the latter, and, as mentioned above, it is also obtained in the preparation of perezinone, and by the action of alcoholic aniline on the substance $C_{15}H_{16}O_4$, melting at 166—167°. It crystallises from alcohol in bronze-coloured needles, and gives on analysis figures which are not readily to be explained. It contains no nitrogen:

0·1036 gave 0·2612 $CO_2$ and 0·0510 $H_2O$. C = 68·76; H = 5·5.
0·1058 „ 0·2660 $CO_2$ „ 0·0546 $H_2O$. C = 68·6; H = 5·7.

It is readily soluble in dilute sodium hydroxide, giving a red solution, and also in sodium carbonate. No colour is given with ferric chloride. Zinc dust and acetic acid easily reduce it to a colourless solution, which, however, rapidly resumes its former red colour on keeping in the air, thus resembling perezone; like the latter it is also not reduced by sulphurous acid. The quinone structure is therefore probably present.

### *Attempted Acetylation of Hydroxy- and Amino-perezone.*

Anschütz and Leather failed to obtain a crystalline acetyl derivative of hydroxyperezone, and the author has found that, although acetic anhydride appears to react with this substance, only a pale coloured glue could be obtained. This glue closely resembled that produced by the action of acetic anhydride on perezone, and the fact that both were without any characteristic quinone colour makes it conceivable that a rearrangement of the atoms in the molecule of hydroxyperezone is brought about by this treatment just as occurred in the case of perezone itself. It was therefore much to be regretted that a crystalline compound could not be obtained in order to obtain further evidence on this point.

Aminoperezone with acetic anhydride also gave a similar clear gum, from which no crystalline product could be obtained. When boiled in alcoholic solution with zinc chloride, aminoperezone forms an additive product, which crystallises from alcohol as a blue powder, and contains chlorine. It appears to be the *zincichloride*:

0·1206 gave 0·0148 ZnO. Zn = 9·86.

$(C_{15}H_{21}O_3N)_2ZnCl_2$ requires Zn = 9·87 per cent.

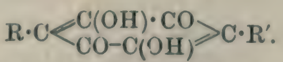
### *Various Experiments with Perezone.*

Attempts were made to isolate the colourless reduction product through its acetyl compound by boiling perezone in acetic anhydride with zinc dust. In all cases, however, the whole of the acid was recovered unchanged, being oxidised back by the air. Many experiments were made with a view to obtaining some clue to the constitution of the side-chains by oxidising with potassium permanganate, potassium dichromate, etc., and by fusion with potassium hydroxide, but no crystalline compound could ever be isolated. A non-crystalline acid portion, which had a strong odour resembling that of butyric acid, and traces of a phenolic substance were the only indications obtained during these oxidations and fusion experiments; also a characteristic sweet odour was always noticed, which somewhat resembled that of amyl acetate.

Attempts at benzoylating perezone by the normal Schotten-Baumann method were entirely without success, and this is not surprising, seeing that attempts at acetylation by boiling with acetic anhydride and fused sodium acetate or acetyl chloride under ordinary pressure were also unsuccessful.

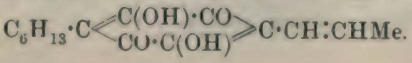
### *Addendum.*

Fichter, Jetzer, and Leepin (*Annalen*, 1913, **395**, 15) have now shown that hydroxyperezone has the properties of a 3 : 6-dihydroxy-2 : 5-dialkyl-*p*-benzoquinone:



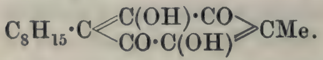
$$\mathrm{R\cdot C}\begin{array}{c}\diagup\ \mathrm{C(OH)\cdot CO}\ \diagdown\\ \diagdown\ \mathrm{CO{-}C(OH)}\ \diagup\end{array}\mathrm{C\cdot R'}.$$

and that it yields $\alpha\beta$-diketobutyric acid on treatment with ozonised oxygen. The latter result is accounted for by the suggestion that $R^1$ = propenyl, and R must then be hexyl, since $R + R^1 = C_9H_{17}$. Hydroxyperezone would then have the following constitution:



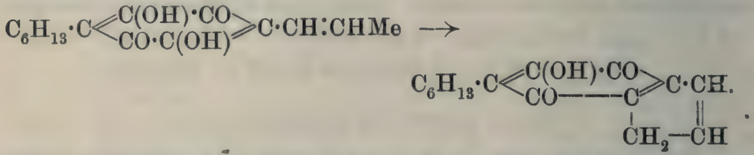
$$\mathrm{C_6H_{13}\cdot C}\begin{array}{c}\diagup\ \mathrm{C(OH)\cdot CO}\ \diagdown\\ \diagdown\ \mathrm{CO\cdot C(OH)}\ \diagup\end{array}\mathrm{C\cdot CH{:}CHMe}.$$

It should be pointed out, however, that the formation of **$\alpha\beta$**-diketobutyric acid can be explained at least equally well by the assumption that $R^1$ = methyl, when R would be octenyl, as follows:



$$C_8H_{15}\cdot C\left<\begin{matrix}C(OH)\cdot CO\\ CO\cdot C(OH)\end{matrix}\right>CMe.$$

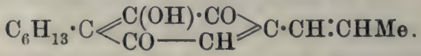
Fichter, Jetzer, and Leepin explain the formation of perezinone, which is obtained by the dehydration of hydroxyperezone with concentrated sulphuric acid by the assumption that the following condensation takes place:



$$C_6H_{13}\cdot C\left<\begin{matrix}C(OH)\cdot CO\\ CO\cdot C(OH)\end{matrix}\right>C\cdot CH{:}CHMe \longrightarrow$$

$$C_6H_{13}\cdot C\left<\begin{matrix}C(OH)\cdot CO\\ CO\text{———}C\end{matrix}\right>C\cdot CH. \quad \begin{matrix}| & \| \\ CH_2\text{—}CH\end{matrix}$$

Since perezone does not undergo a similar dehydration with sulphuric acid, they ascribe to it the formula:



$$C_6H_{13}\cdot C\left<\begin{matrix}C(OH)\cdot CO\\ CO\text{——}CH\end{matrix}\right>C\cdot CH{:}CHMe.$$

The evidence for the nature of the side-chains is, however, inconclusive, and this constitutional formula can therefore only be accepted with reserve.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

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## CXVII.—*The Absorption Spectra of Various Derivatives of Benzene.*

By JOHN EDWARD PURVIS and NIAL PATRICK McCLELAND.

THE aim of this communication is to describe a series of observations of the absorption spectra in the ultra-violet regions of various derivatives of benzene in various physical conditions, and particularly the vapours of these substances, and to see how far the absorption is modified when different side chains are introduced, and especially the nitro-group.

The substances examined were the following: phenol, catechol, guaiacol, *o*-, *m*-, and *p*-cresols, *o*-, *m*-, and *p*-chlorophenols, *o*-, *m*-, and *p*-chloroanilines, benzaldehyde, acetophenone, benzophenone, nitrobenzene, *o*-, *m*-, and *p*-dinitrobenzenes, *o*-, *m*-, and *p*-nitrotoluenes, *o*-nitrophenol, *o*- and *p*-nitroanisoles, *o*-nitroaniline, *o*-, *m*-, and *p*-nitrobenzaldehydes, and nitromethane. In some cases it was impossible to examine the vapours of the isomerides because of their comparatively high melting points.

The experimental methods have been described before. The cadmium spark and the acetylene lamp were used as sources of the radiant energy.

*Phenol.*—Hartley, Dobbie, and Lauder (T., 1902, **81**, 929) showed that solutions of the substances had one strong band, the head of which is at about 1/λ 3670 (λ 2720). This was confirmed later by Baly and Ewbank (T., 1905, **87**, 1347).

The vapour of this substance has been studied by the authors, and the following phenomena were observed at the temperatures of 45° and 60° in a 200 mm. tube.

*Abbreviations:* v.w. = very weak; w. = weak; f.str. = fairly strong; str. = strong; diff. = diffuse.

|  | 45°. 70 mm. λ |
|---|---|
| A | 2812 v.w. |
|  | 2794 ,, |
|  | 2790 w. |
|  | 2784 v.w. |
| B | 2777 ,, |
|  | 2775 ,, |
|  | 2771 ,, |
|  | 2766 w. |
|  | 2761 w. |
|  | 2757 v.w. |
|  | 2755 w. |
|  | 2751 f.str. |
| C | 2749 v.w. |
|  | 2744 ,, |
|  | 2738 ,, |
|  | 2735 ,, |
|  | 2732 ,, |
|  | 2729 w. |
|  | 2725 w. |
|  | 2722 w. |
|  | 2719 w. |
|  | 2716 w. |
|  | 2710 f.str. |
| D | 2708 w. |
|  | 2704 w. |
|  | 2700 w. |
|  | 2695 w. |
|  | 2691 w. |
|  | 2689 str., wide |
|  | 2687 ,, |
| D′ | 2681 w. |
|  | 2677 w. |
|  | 2672 str. |
|  | 2669 w. |
|  | 2663 v.w. |
|  | 2659 ,, |
|  | 2651 diff. |
|  | 2650 v.w. |
|  | *2644 str. |
|  | 2641 v.w. |
|  | 2638 ,, |
|  | *2634 f.str. |
|  | 2631 v.w. |
|  | 2630 ,, |
|  | 2628 ,, |
|  | *2625 str |
|  | 2623 v.w. |
|  | 2618 w. |
|  | *2613 str. |
|  | 2611 w. |
|  | 2607 w. |
|  | *2604 f. str. |
|  | 2603 w. |
|  | 2597 ,, |
|  | *2593 f.str. |
|  | *2580 str. |
|  | 2578 v.w. |
|  | 2575 ,, |
|  | *2572 f. str. |
|  | 2565 v. w. |
|  | *2560 w. |
|  | 2558 v.w. |
|  | *2552 f. str. |
|  | 2549 v.w. |
|  | *2540 ,, |
|  | *2530 w. |
|  | 2529 v.w. |
|  | 2521 ,, |
|  | *2520 w. |
|  | 2518 ,, |
|  | 2516 ,, |
|  | 2514 ,, |
|  | 2510 ,, |
|  | 2509 ,, |
|  | 2504 ,, |
|  | 2500 ,, |

General absorption began at λ 2180.

76 bands.

| 60°. 100 mm. λ |  |
|---|---|
| 2812 v.w. |  |
| 2801 ,, |  |
| 2794 ,, |  |
| 2788 w., wide |  |
| 2784 ,, |  |
| 2780 v.w. |  |
| 2777 ,, |  |
| 2775 ,, wide |  |
| 2769 w. |  |
| 2766 f. str. |  |
| 2761 ,, |  |
| 2760 to 2748 str. |  |
| 2744 v.w. |  |
| 2738 ,, |  |
| 2735 ,, |  |
| 2732 ,, |  |
| 2729 w. |  |
| 2725 w. |  |
| 2722 w. |  |
| 2719 w. |  |
| 2716 w. |  |
| 2710 str., wide |  |
| 2704 to 2670 very diff. |  |
| 2663 | These bands can be distinguished through a broad belt of diffuse continuous spectrum. |
| 2651 |  |
| 2644 |  |
| 2641 |  |
| 2638 |  |
| 2635 |  |
| 2625 |  |
| 2623 to 2600 |  |
| 2593 |  |
| 2580 |  |
| 2578 |  |
| 2575 |  |
| 2572 |  |
| 2565 str. |  |
| 2560 w. |  |
| 2558 w. |  |
| 2552 w. |  |
| 2549 w. |  |
| 2540 w. |  |
| 2530 v.w. |  |
| 2529 ,, |  |
| 2521 ,, |  |
| 2520 ,, |  |
| 2518 ,, |  |
| 2516 ,, |  |
| 2514 ,, |  |
| 2510 ,, |  |
| 2509 ,, |  |
| 2504 ,, |  |
| 2500 ,, |  |

General absorption began at λ 2220

53 bands.

It is seen that the absorption spectrum of the vapour of phenol consists of a maximum number of 76 bands, which, with increasing temperature, coalesce into a single band resembling that observed in the solution. The spectrum does not show any resemblance to that of benzene, as described and measured by Hartley (*Phil. Trans.*, 1907, *A*, **208**, 475). The hydroxyl group has entirely changed the type of vibration of the system, as does the amino-group in aniline (Purvis, T., 1910, **97**, 1546).

The most marked feature of the spectrum is the long series of equidistant bands marked * in the table. These bands are very similar in appearance (save that the more refrangible ones are weaker), and are situated about 10 units apart. If the spectra of phenol and of anisole (Purvis and McCleland, T., 1912, **101**, 1514) be compared it will be found that these bands, with only two exceptions, appear in the two spectra. The anisole bands are, however, slightly wider than those in phenol. The two spectra show very close resemblance in most respects, and, with the dispersion used, it does not appear that there is any appreciable shift.

It should be added that the spectrum of anisole (Baly and Ewbank, *loc. cit.*), in solution, is described as having two bands, whereas that of phenol has only one.

*Catechol.*—Hartley has shown (T., 1888, **53**, 651) that solutions of the substance have one large strong band, the head of which is about at 1/λ 3660 (λ 2730).

The substance was placed in a 100 mm. tube, which was exhausted, so that the inside pressure was about 12 mm. It was then examined at various temperatures, and the following phenomena were observed:

| 90°. | 100°. |
|---|---|
| λ | |
| 2806 w. | As described at 90°, but the bands were stronger. |
| 2804 w. | |
| 2797 w. | |
| 2794 w. | General absorption began at λ 2250. |
| 2789 to 2784 w. diff. | 6 bands. |
| 2736 | |
| General absorption began at λ 2240. | |
| 6 bands. | |

*Guaiacol.*—Baly and Ewbank (*loc. cit.*) showed that the solution of the substance has one band, the head of which is at about 1/λ 3610 (λ 2770).

As the melting point of the substance is considerably lower than that of catechol, its vapour was much more easily examined. The substance was placed in a 200 mm. tube, and examined at various temperatures and pressures. The following phenomena were observed:

| 45°. | 60°. | 75°. | 90°. |
|---|---|---|---|
| 833 mm. | 863 mm. | 893 mm. | 923 mm. |
| The rays were weak between λ 2797 and λ 2783.<br>λ<br>2754 v.w.<br>2725 v.w., diff.<br>2709 w.<br>2688 f.str., narr.<br>2674 w. narr.<br>General absorption. began at λ 2150<br>6 bands. | λ<br>2833 v.w., diff.<br>2822 ,, ,,<br>2816 to 2783 str., diff.<br>The rays were then weakly absorbed, but the following bands showed through:<br>2754 w.<br>2744 to 2607 v. diff.<br>General absorption began at γ 2240.<br>4 bands and 1 stronger band. | 2841 v.w., diff.<br>2840 to 2578 strong band.<br>General absorption began at λ 2280.<br>1 weak band and 1 very strong band. | Rays were absorbed between λ 2880—λ 2495<br>General absorption began at λ 2400.<br>1 strong band. |

There are therefore a series of fine bands in the vapour of the substance, which, at the higher temperatures and pressures, coalesce into a single large band comparable with the solution band. The total number of bands is much less than was found in the vapour of phenol.

*Quinol.*—Hartley and Leonard (T., 1909, **95**, 34) describe a narrow band at λ 2538, and broad bands between λ 2396 to 2332 and λ 3080 to 2575 in the vapour spectrum of this substance.

o-, m-, and p-*Cresols.*—The absorption spectra of solutions of each of these substances have been shown by Hartley (T., 1888, **53**, 641) to exhibit one large band, the head of which is at about 1/λ 3650 (λ 2740).

o-*Cresol.*—The absorption spectra of the vapour of the substance in a 200 mm. tube and at various temperatures and pressures showed the following phenomena:

| 45°. | 60°. |
|---|---|
| 829 mm. | 859 mm. |
| λ<br>2825 w.<br>The rays were weak between 2775 and 2757.<br>2695 v.w.<br>2686 f.str.<br>2673<br>General absorption began at λ 2190.<br>5 bands. | λ<br>2825 w.<br>2781 to 2751 f.str.<br>2743 str.<br>2732 to 2580<br>General absorption began at λ 2225.<br>3 weaker bands and 1 large band. |

m-*Cresol.*—The absorption spectra of the vapour of the substance in a 200 mm. tube and at various temperatures and pressures showed the following phenomena:

| 45°. 835 mm. λ | | 60°. 865 mm. λ | |
|---|---|---|---|
| 2778 | f. str. | 2820 to 2760 | str. |
| 2771 | ,, | 2754 | v.w., diff. |
| 2766 | ,, | 2745 to 2568 | v. str. |
| 2754 | v.w. | | |
| 2732 to 2691 | v.w., diff. | | |
| 2684 | v.w., wide | | |
| 2644 | v.w. | | |
| 2638 | ,, | | |
| 2633 | ,, | | |
| 2630 | ,, | | |
| 2623 | ,, | | |
| 2618 | ,, | | |

45°: General absorption began at λ 2190.

12 bands.

60°: General absorption began at λ 2250.

2 weaker bands and 1 large strong band.

p-*Cresol.*—The absorption spectra of the vapour of the substance in a 200 mm. tube, and at various temperatures and pressures, showed the following phenomena:

| 45°. 296 mm. λ | |
|---|---|
| 2850 | v.w. |
| 2841 | v.w., narr. |
| 2840 | ,, ,, |
| *2828 | str. diff. on less refrangible side |
| 2823 | w. |
| *2807 to 2794 | str. diff. on less refrangible side. |
| *2775 to 2760 | str. diff. on less refrangible side. |
| 2733 | w. |
| 2728 | v.w. |
| 2709 * to 2702 | w., wide |
| 2699 | v.w. |
| 2680 * to 2664 | w., wide |
| 2647 * to 2630 | w., wide |
| 2626 | v.w., narr. |
| 2623 | ,, |
| 2620 | ,, |
| 2618 * to 2603 | v.w., diff. |
| 2590 * to 2577 | v.w., diff. |

General absorption λ 2200.

18 bands.

| 60°. 326 mm. λ | |
|---|---|
| 2869 | v.w. |
| 2850 | f. str. |
| 2841 | w. |
| 2840 | w. |
| *2837 to 2820 | str. |
| 2823 | w. |
| 2812 | v.w. |
| 2808 | ,, |
| *2807 to 2794 | f. str. |
| 2782 | v.w., diff. |
| 2778 | ,, ,, |
| *2775 to 2759 | str. |
| 2741 * to 2732 | f. str. |

60°. 326 mm.

The rest of the bands were as described at 45°, but at 60° they appeared stronger.

General absorption λ 2260.

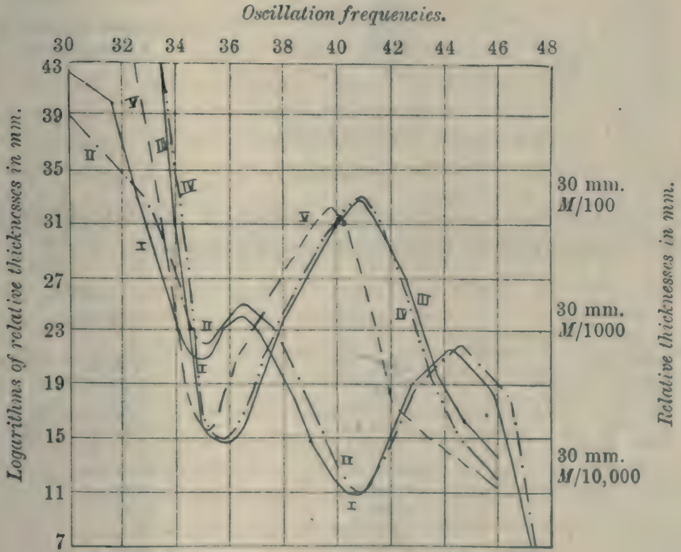
23 bands.

The bands marked * are wide and sharp on the more refrangible side. They appear to correspond with the bands marked similarly in phenol, but are much wider.

The vapour bands are wholly unlike the single solution band of each of these substances, although at the higher temperatures and pressures there is a tendency for these bands to coalesce into one large band not unlike the solution band. Also, it should be noticed that the vapour bands in each of the substances are much fewer in number than in phenol vapour; the spectrum of the para-derivative alone shows a marked resemblance to that of the parent substance; and that of the meta-derivative, and, still more, that of the ortho-compound, appear to be quite unlike it.

o-, m-, and p-*Chlorophenols.*—Alcoholic solutions of various strengths were examined, and a large band was found in solutions of each of the substances. The absorption curve (Fig. 1, III, IV, and V) show that the head of the curve of the ortho-compound is at 1/λ 3580 (λ 2790); that of the meta-compound is at 1/λ 3590 (λ 2784); and that of the para-compound at 1/λ 3500 (λ 2856). The band of the *p*-compound is therefore shifted a little more towards the red end of the spectrum than the bands of the other isomerides. The general form of the bands is very similar to the large band of phenol.

FIG. 1.



I. *Benzaldehyde.*
II. *Acetophenone* (dash and dot line).
III. o-*Chlorophenol.*
IV. m-*Chlorophenol* (dash and two dots line).
V. p-*Chlorophenol* (broken line).

o-*Chlorophenol.*—The absorption spectra of the substance in a 200 mm. tube at various temperatures and pressures showed the following phenomena:

| 30°.<br>813 mm.<br>λ | 30°.<br>813 mm.<br>λ | 45°.<br>839 mm.<br>λ |
|---|---|---|
| 2809 f.str. | 2653 w., diff. | 2870 v.w., diff. |
| 2807 v.w. | 2643 ,, | 2853 w. |
| 2804 | 2630 ,, | 2840 w. |
| to str. | 2623 ,, | 2830 |
| 2775 | 2616 ,, | to v. str. |
| 2767 v.w. | 2612 ,, | 2564 |
| 2763 ,, | 2608 ,, | |
| 2760 ,, | 2604 ,, | General absorption began at λ 2270. |
| 2755 ,, | 2601 ,, | |
| 2752 ,, | 2593 ,, | |
| 2735 w. | 2581 ,, | 3 narrow bands and 1 strong band. |
| 2734 | 2578 ,, | |
| to w. diff. | 2571 ,, | |
| 2677 | | |
| 2671 ,, | General absorption began at λ 2240. | |
| | 24 bands. | |

m-*Chlorophenol.*—The absorption spectra of *m*-chlorophenol in a 200 mm. tube at various temperatures and pressures:

| 45°.<br>839 mm.<br>λ | 60°.<br>869 mm.<br>λ | 60°.<br>869 mm.<br>λ |
|---|---|---|
| 2809 v.w. | 2815 v.w. | 2725 w. |
| 2805 v.w., narr. | 2809 w. | 2722 w. |
| 2802 w., wide | 2805 w. | 2717 w. |
| 2798 w. | 2802 f.str. | 2713 v.w., diff. |
| 2795 f.str. | 2798 ,, | 2707 v.w. |
| 2789 v.w. | 2795 str. | 2704 ,, |
| 2784 f.str. | 2792 w. | 2692 ,, |
| 2781 v.w. | 2789 w. | 2685 ,, |
| 2756 ,, | 2784 str. | 2679 ,, |
| 2733 ,, | 2781 w. | 2674 ,, |
| 2725 ,, | 2777 v.w. | 2664 ,, |
| 2717 ,, | 2756 f.str. | 2657 ,, |
| 2653 ,, | 2743 w. | |
| General absorption began at λ 2130. | 2738 v.w. | General absorption began at λ 2235. |
| | 2733 f.str. | |
| | 2728 v.w. | |
| 13 bands. | | 28 bands. |

p-*Chlorophenol.*—The absorption spectra of *p*-chlorophenol in a 200 mm. tube at various temperatures and pressures:

| 45°.<br>839 mm.<br>λ | 45°.<br>839 mm.<br>λ |
|---|---|
| 2875 v.w. | 2785 v.w. |
| 2873 w. | 2781 ,, |
| 2844 v.w. | General absorption began at λ 2150. |
| 2841 ,, | |
| | 6 bands. |

| 60°. 869 mm. λ | 60°. 869 mm. λ. | 60°. 869 mm. λ |
|---|---|---|
| 2916 w. | 2813 w. | 2753 v.w. |
| 2905 v.w. | 2809 w. | 2722 ,, |
| 2897 ,, | 2807 w. | 2707 v.w., wide |
| 2894 ,, | 2803 w. | 2704 ,, ,, |
| 2882 to 2875 f. str. | 2794 v.w. | 2698 ,, ,, |
| | 2788 v.w. | 2686 ,, ,, |
| | 2785 f.str. | |
| 2873 f.str. | 2781 v.w. | General absorption began at λ 2260. |
| 2869 w. | 2779 ,, | |
| 2866 v.w. | 2770 ,, | |
| 2860 ,, | 2756 w. | 30 bands. |
| 2849 w. | | |
| 2844 w. | | |
| 2841 w. | | |

Therefore the absorption spectra of the vapours of *o*-, *m*-, and *p*-chlorophenols are again wholly different from those of the one band of each of the solutions; but, at the higher temperatures and pressures, there is a tendency for the vapour bands to coalesce into one large band which is similar to the solution band. The total number of bands is considerably reduced as compared with those of phenol, as a consequence of the introduction of the chlorine atom. Of the three isomerides, the spectrum of the para-, and still more of the meta-compound, appears to resemble that of the parent substance; but there is a shift of about 50 units towards the less refrangible part of the spectrum.

o-, m-, *and* p-*Chloroanilines.*—Baly and Ewbank (T., 1905, **87**, 1355) showed that in acid solutions of *o*-chloroaniline there was a rapid extension of the rays between about 1/λ 3700 to 1/λ 4300 (λ 2700 to λ 2320); in *m*-chloroaniline there was a band the head of which was at 1/λ 3700 (λ 2700); and in *p*-chloroaniline there were two bands at 1/λ 3650 (λ 2740), and at 1/λ 3750 (λ 2660); whereas in neutral solutions of each of these substances the ortho-compound showed a band at 1/λ 3450 (λ 2900), the meta-compound one at 1/λ 3410 (λ 2930), and the para-compound at 1/λ 3360 (λ 2980).

o-*Chloroaniline.*—The absorption spectrum of the vapour of *o*-chloroaniline in a 200 mm. tube at various temperatures and pressures:

| 30°. 801 mm. λ | 30°. 801 mm. λ |
|---|---|
| 2980 w. | 2817 v.w., diff. |
| 2970 v.w., narr. | 2809 ,, ,, |
| 2956 v.w. | |
| 2954 ,, | The rays were then transmitted to λ 2370, beyond which only the strong Cd. lines were visible. |
| 2946 ,, | |
| 2933 ,, | |
| 2905 w., wide | |
| 2880 ,, | |
| 2869 v.w. | 12 bands. |
| 2825 v.w., diff. | |

45°.
827 mm.

| λ | |
|---|---|
| 2995 | w., narr. |
| 2978 | f.str., wide |
| 2970 | v.w., narr. |
| 2966 to 2960 | diffuse |
| 2958 to 2950 | f.str. |

45°.
827 mm.

| λ | |
|---|---|
| 2948 to 2945 | f.str. |

Rays were then absorbed to λ 2775. They were then transmitted to λ 2460, where general absorption began.

7 weaker bands and 1 large band.

m-*Chloroaniline*.—The absorption spectrum of the vapour of *m*-chloroaniline in a 200 mm. tube at various temperatures and pressures:

45°.
829 mm.

| λ | |
|---|---|
| 2995 | v.w., narr. |
| 2981 | w., narr. |
| 2978 | f.str. |
| 2961 | w. |
| 2956 | w. |
| 2952 | w. |
| 2946 | w. |
| 2941 | w. |
| 2938 | v.w. |
| 2932 | f.str. |
| 2927 | v.w. |
| 2924 | ,, |
| 2920 | ,, |
| 2914 | ,, |
| 2910 | w. |
| 2906 | w. |

45°.
829 mm.

| λ | |
|---|---|
| 2898 | v.w. |
| 2893 | ,, |
| 2890 | w. |
| 2875 | v.w. |
| 2870 | ,, |
| 2857 | v.w., diff. |
| 2849 | ,, ,, |
| 2846 | ,, ,, |

General absorption began at λ 2260.

24 bands.

60°.
859 mm.

| λ | |
|---|---|
| 3002 | v.w. |
| 3000 | w., narr. |
| 2995 | ,, |
| 2986 | ,, |
| 2981 | f.str. |
| 2978 | str. |
| 2963 | v.w. |
| 2961 | f.str. |
| 2956 | ,, |
| 2952 | str., wide |
| 2946 | w. |
| 2941 | mod. w. |
| 2938 | ,, |
| 2932 | str. |
| 2927 | w. |
| 2924 | w. |

60°.
859 mm.

| λ | |
|---|---|
| 2920 | w. |
| 2914 | w. |
| 2910 | f.str., wide |
| 2906 | ,, ,, |
| 2898 | w. |
| 2893 | w. |
| 2890 | str. |

Then faint absorption to λ 2780.

General absorption began at λ 2490.

23 bands and 1 strong band.

p-*Chloroaniline*.—The absorption spectra of the vapour of *p*-chloroaniline in a 200 mm. tube at various temperatures and pressures:

60°.
857 mm.

| λ | |
|---|---|
| 3174 | w. |
| 3147 | f.str., diff. |
| 3144 | w., narr. |
| 2969 | f.str. |

General absorption began at λ 2500.

4 bands.

75°.
887 mm.

| λ | |
|---|---|
| 3174 | w. |
| 3155 to 3040 | str., wide. |
| 3035 | w., diff. |

3032 to 2800 a broad diffuse band, the less refrangible edge of which is apparently broken up into smaller bands, but the nature of the cadmium spark in this region makes accurate measurement impossible.

4 weaker bands and 1 large band.

The vapour of each of these substances hence shows a series of fine bands completely different from their solution; but the number of vapour bands in each substance is less than in the vapour of aniline. The striking shift of the vapour bands of these aniline compounds towards the red end, as compared with other benzene derivatives, is comparable with that noticed in the vapour of aniline itself (Purvis, *loc. cit.*), and this appears to be a clear indication that the amino-group is a powerful oscillation centre.

As in the phenols, the meta-derivative spectroscopically resembles the parent substance more than do the other isomerides, whilst the ortho- is quite distinct. The shift due to the chlorine atom in the meta-chloroaniline is about 37 units, and when this allowance is made it is found that a large number of the principal bands in the spectrum correspond with similar bands in aniline. Further, the bands of *m*-chloroaniline are much sharper than those of the other isomerides.

*Benzaldehyde.*—Baly and Collie (T., 1905, **87**, 1332) found a band at 1/λ 3500 (λ 2850) in *M*/1000-alcoholic solutions. We have repeated these experiments and also investigated the absorption of *M*/10,000-solutions, and find that besides the less refrangible band noticed by Baly and Collie in *M*/1000-solutions, there is a large band the head of which is at 1/λ 4070 (λ 2456) in *M*/10,000-solutions. The absorption curve has been drawn (Fig. 1, I). The benzaldehyde was redistilled under diminished pressure and dissolved in alcohol which had been previously boiled in order to hinder the oxidation to benzoic acid. The absorption spectra of the vapour of benzaldehyde at various temperatures and pressures in a 200 mm. tube showed the following phenomena. The vapour of this substance was examined both with the acetylene light and also with the cadmium spark. Owing to the ease with which it oxidises, the vapour was examined in an atmosphere of nitrogen. Further, the vapour of carefully purified benzoic acid was found to show none of the bands given below:

| 30°. | 30°. | 30°. | 30°. |
|---|---|---|---|
| 799 mm. | 799 mm. | 799 mm. | 799 mm. |
| λ | λ. | λ | λ |
| 2860 w. | 2784 w. | 2711 v.w., diff. | 2620 v.w. |
| 2850 f.str. | 2776 f.str. | 2707 ,, ,, | 2615 ,, |
| 2840 ,, | 2771 w. | 2701 v.w. | |
| 2831 ,, | 2762 f.str. | 2688 ,, | The rays were also absorbed between λ 2455 and λ 2160. |
| 2822 ,, | 2757 w. | 2680 ,, | |
| 2815 ,, | 2752 v.w. | 2667 ,, | |
| 2807 ,, | 2743 ,, | 2653 ,, | |
| 2801 w. | 2729 v.w., diff. | 2633 ,, | |
| 2796 f.str. | 2720 ,, ,, | 2622 ,, | General absorption began at λ 2150. |
| 2790 w. | | | |
| | | | 31 bands. |

45°.
825 mm.

| λ | |
|---|---|
| 3700 | v.w. |
| 3587 | ,, |
| — | |
| 2894 | v.w. |
| 2886 | ,, |
| 2877 | ,, |
| 2870 | ,, |
| 2860 | f. str. |
| *2850 | v.str. |
| *2840 | ,, |
| *2831 | str. |

45°.
825 mm.

| λ | |
|---|---|
| *2822 | str., wide |
| *2815 | ,, |
| *2807 | ,, |
| 2801 | w. |
| *2796 | f.str. |
| 2790 | w. |
| 2784 | w. |
| *2776 | str. |
| 2771 | w. |
| *2762 | str. |
| 2757 | w. |

45°.
825 mm.

| λ | |
|---|---|
| 2752 | w. |
| 2743 | w. |
| 2729 | v.w., diff. |
| 2720 | ,, ,, |
| 2711 | ,, ,, |
| 2707 | ,, |
| 2701 | w. |
| 2688 | w. |
| 2680 | v.w. |
| 2667 | w. |

45°.
825 mm.

| λ | |
|---|---|
| 2653 | v.w. |
| 2633 | ,, |
| 2622 | ,, |
| 2620 | ,, |
| 2615 | ,, |

General absorption began at λ 2480.

36 bands.

75°.
885 mm.

| λ | |
|---|---|
| 3700 | v.w. |
| 3695 | f.str. |
| 3650 | v.w. |
| 3608 | ,, |
| 3550 | ,, |
| 3515 | f.str. |
| 2949 | v.w. |
| 2941 | ,, |
| 2929 | w. |

75°.
885 mm.

| λ | |
|---|---|
| *2894 | f.str. |
| *2886 | ,, |
| 2885 | w. |

General absorption began at λ 2880.

12 bands.

The bands marked * are very similar in appearance; they are diffuse on the less refrangible side, and are not unlike the similar series of bands in phenol. The vapour of the substance, therefore, showed two series of fine bands which are quite different from the less refrangible solution band. On the other hand, the more refrangible vapour band between λ 2430 and λ 2220 is comparable with the large solution band at 1/λ 4070 (λ 2456) in that it does not break up into a series of finer bands; and differs from it mainly in position. However, the series of fine bands on the border of the visible region does not appear to be strong enough to appear in the solution spectrum.

*Acetophenone.*—Baly and Collie (*loc. cit.*) noticed a rapid extension of the rays between 1/λ 3500 (λ 2856) and 1/λ 3800 (λ 2630) in *M*/1000-alcoholic solutions. The authors have repeated these experiments and also investigated the absorption of *M*/10,000-solutions, and find that, besides the much less refrangible band in *M*/1000-solutions noticed by Baly and Collie, there is a large band at 1/λ 4080 (λ 2450) in *M*/10,000-solutions. The absorption curve has been drawn (Fig. 1, II).

The absorption spectra of the vapour of acetophenone at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| 30°.<br>801 mm.<br>λ | 60°.<br>857 mm.<br>λ |
|---|---|
| The rays were absorbed between λ 2420 and λ 2200, and then weakly transmitted to λ 2150, where general absorption began. | 2833 to 2816 } diff.<br>2763 to 2700 } diff. |
| | General absorption began at λ 2460. |

The vapour of acetophenone thus consists of two principal bands, the less refrangible of which breaks up into two smaller bands. The vapour was also examined for bands in the neighbourhood of the visible part of the spectrum, but no absorption was detected. It is seen that the number of bands found in the vapour of benzaldehyde has been considerably decreased.

*Benzophenone.*—The authors (T., 1912, **101**, 1514) found two solution bands at 1/λ 2960 (λ 3360) and 1/λ 3980 (λ 2510) respectively. The latter was visible in $M$/10,000-alcoholic solutions, and the former in $M$/100-solutions.

The absorption spectra of the vapour at various temperatures and pressures showed the following phenomena:

| $t$°. | Pressure in mm. | |
|---|---|---|
| 90 | 927 | The rays were absorbed between λ 2530—λ 2320, and then weakly transmitted to about λ 2150. |
| 100 | 943 | The rays were transmitted to λ 2550. |

The authors were not successful in obtaining sufficient vapour in the tube to show a vapour band corresponding with the very weak solution band at λ 3360. The more refrangible band showed no signs of breaking up into a series of finer bands, and it corresponds with the solution band λ 2510. It should also be noticed that all the fine bands found in the vapour of benzaldehyde have completely disappeared.

*Nitrobenzene.*—Pauer (*Ann. Phys. Chem.*, 1897, [iii], **61**, 375) found no bands in alcoholic solutions of this substance. Baly and Collie (T., 1905, **87**, 1344) found a weak band as indicated by a rapid extension of the transmitted rays between 1/λ 3700 and 1/λ 4200 (λ 2702—λ 2380) in $M$/1000-alcoholic solutions. The authors have repeated the experiments, and the absorption curve of this very weak band has been drawn (Fig. 2, I) in order to compare it with the dinitrobenzenes.

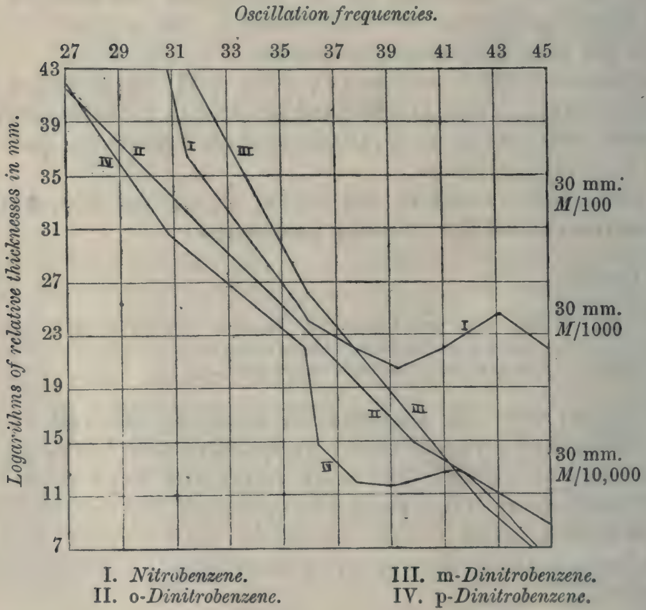
The absorption spectrum of the vapour of nitrobenzene at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure in mm. | |
|---|---|---|
| 30 | 797 | The rays were absorbed between about λ 2500—λ 2330 and then transmitted to about λ 2150. The series of Cd lines λ 2329—λ 2144 were fairly well marked. |
| 75 | 883 | The rays were transmitted to about λ 2900. |

The vapour therefore showed a weak band comparable with the weak solution band. All the series of fine bands in benzene vapour described and measured by Hartley (*loc. cit.*) have completely disappeared.

o-, m-, *and* p-*Dinitrobenzenes.*—Alcoholic solutions of each of these substances were examined, and their absorption curves drawn.

FIG. 2.



It will be noticed (Fig. 2, II, III, and IV) that *o*- and *m*-dinitrobenzenes show no bands, whereas *p*-dinitrobenzene shows a very faint band the head of which is at about 1/λ 3900 (λ 2563). The vapours of the dinitrobenzenes were not investigated.

It is interesting to note that Hantzsch and Picton (*Ber.*, 1909, **42**, 2119) found no bands in solutions of trinitrobenzene.

o-*Nitrotoluene.*—Baly, Tuck, and Marsden (T., 1910, **97**, 571) state that solutions of the substance exhibit a band the head of which is at about 1/λ 4000 (λ 2450).

The absorption spectrum of *o*-nitrotoluene vapour at various

temperatures and pressures in a 200 mm. tube showed the following phenomena:

| $t^{\circ}$. | Pressure in mm. | |
|---|---|---|
| 30 | 810 | The rays were transmitted to λ 2150; but they were weak between about λ 2500—λ 2370. |
| 45 | 840 | The rays were transmitted to λ 2590 and then absorbed to about λ 2350; the series of Cd lines λ 2329—λ 2194 were well marked, as well as Cd 2573. |
| 60 | 870 | The rays were transmitted to λ 2900, but the Cd lines λ 2880 and λ 2748 were just visible. |

There was therefore one weak vapour band comparable with the solution band; but there was no resolution of the band into a series of fine bands. The less refrangible regions to about λ 3200 were also examined by using the continuous spectrum of an acetylene lamp, but no bands were observed.

m-*Nitrotoluene.*—Baly, Tuck and Marsden (*loc. cit.*) state that solutions of the substance exhibit a band the head of which is at about 1/λ 3800 (λ 2630). The absorption spectrum of *m*-nitrotoluene vapour at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| $t^{\circ}$. | Pressure in mm. | |
|---|---|---|
| 45 | 830 | The rays were absorbed between λ 2560—λ 2360 and then transmitted to about λ 2140. |
| 90 | 920 | The rays were transmitted to λ 3000. |

There was therefore a single vapour band comparable with the solution band.

p-*Nitrotoluene.*—Baly, Tuck and Marsden (*loc. cit.*) found a band in solutions of the substance the head of which was at 1/λ 3600 (λ 2780). The absorption spectrum of the vapour of *p*-nitrotoluene at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| $t^{\circ}$. | Pressure in mm. | |
|---|---|---|
| 60 | 870 | The rays were absorbed between λ 2650—λ 2360, and then transmitted to λ 2144. The Cd line 2573 was visible. |
| 90 | 930 | The rays were transmitted to λ 2900. |

There was therefore a single vapour band comparable with the solution band. All the finer vapour bands of toluene described and measured by Hartley (*loc. cit.*) have completely disappeared in the vapours of *o*-, *m*-, and *p*-nitrotoluenes.

o-*Nitrophenol.*—Baly, Tuck, and Marsden (*loc. cit.*) found two bands in solutions of the substance the heads of which were 1/λ 2900 (λ 3440) and 1/λ 3600 (λ 2770) respectively.

The absorption spectrum of the vapour of the substance at various

temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure in mm. | |
|---|---|---|
| 45 | 840 | The rays were weakly absorbed between about λ 3450—λ 3100 and again between about λ 2730—λ 2360; and then transmitted to about λ 2190. |
| 60 | 870 | The rays were absorbed between about λ 3600—λ 3020 and then transmitted to about λ 2800. The Cd line 2748 was just visible. |
| 75 | 900 | The rays were absorbed between λ 3750—λ 2990 and then weakly transmitted to λ 2900. |
| 90 | 930 | The rays were transmitted to λ 2850; beyond which there was complete absorption. |

The less refrangible band was also examined at the above temperatures and pressures by means of the continuous spectrum of an acetylene lamp; but there was no resolution of the band into a series of finer bands.

The two vapour bands are, therefore, comparable with the two solution bands, except in position. All the finer bands found in the vapour of phenol have completely disappeared.

o-*Nitroanisole.*—Baly, Tuck, and Marsden (*loc. cit.*) found two bands in solutions of this substance, the heads of which were at about 1/λ 3100 (λ 3220) and 1/λ 4000 (λ 2500) respectively.

The absorption spectrum of the vapour of the substance at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure in mm. | |
|---|---|---|
| 75 | 904 | The rays were transmitted to λ 2200; but they were rather weak between about λ 2430—λ 2350. |
| 90 | 934 | The rays were weakly absorbed between λ 3050—λ 2800; they were transmitted to about λ 2470 and then absorbed to λ 2330; and then transmitted to λ 2250. |
| 100 | 950 | The rays were fairly well absorbed between λ 3100—λ 2730, although several of the strong Cd lines were visible in this region; they were then transmitted to about λ 2550, after which there was absorption to the Cd lines 2329, 2321, and 2313 which were visible. |

There were, therefore, two vapour bands which are comparable with the two solution bands, except in position. All the series of finer bands found by the authors in the vapour of anisole (T., 1912, **101**, 1514) have completely disappeared.

p-*Nitroanisole.*—Solutions of this substance have not been examined, but Baly, Tuck and Marsden (*loc. cit.*) have examined *p*-nitrophenetole, and they found one band the head of which is at about 1/λ 3400 (λ 2940).

The absorption spectrum of the vapour of *p*-nitroanisole at various

temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure in mm. | |
|---|---|---|
| 75 | 904 | The rays were absorbed between λ 2900—λ 2600 and then transmitted to λ 2190. The Cd line 2748 was fairly well marked. |
| 100 | 950 | The rays were absorbed between λ 3000—λ 2330. The Cd lines 2329 to 2265 were well marked. |

There was therefore only one large vapour band.

o-*Nitroaniline.*—Alcoholic solutions of the substance of various strengths were examined, and the curve drawn (Fig. 3, IV). There are two bands: a large, strong one in the visible part of the spectrum, the head of which is at 1/λ 2450 (λ 4080), and a second, very weak one, the head of which is at 1/λ 3570 (λ 2800).

The absorption spectrum of the vapour of *o*-nitroaniline at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure. in mm. | |
|---|---|---|
| 90 | 926 | The rays were transmitted to about λ 2420; but they were somewhat weak between λ 3650—λ3350; and again between λ 2420—λ 2350. The series of Cd lines 2329—2194 was well marked. |
| 100 | 942 | The rays were very weak between λ 3800—λ 3300, and then transmitted to λ 2450; the Cd lines 2329, 2321, 2313 were also easily seen. |

The vapour was also examined in the less refrangible regions at the above temperatures and pressures by using the continuous spectrum of an acetylene lamp, but no fine bands were observed. The results show the presence of two bands, the more refrangible one being very faintly indicated, and there was no resolution into a series of finer bands. All the fine bands found and measured in the vapour of aniline (Purvis, *loc. cit.*) have completely disappeared.

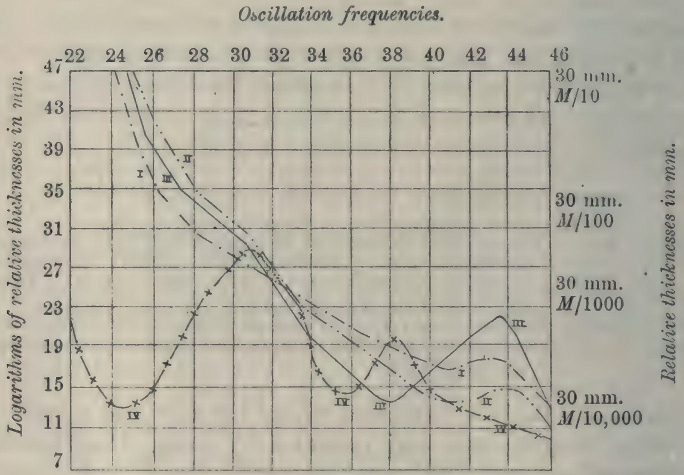
o-, m-, *and* p-*Nitrobenzaldehydes.*—Alcoholic solutions of these substances were examined, and their absorption curves drawn (Fig. 3, I, II, and III). The ortho-compound shows a very weak, shallow band, the head of which is at about 1/λ 4100 (λ 2438); it is more like a very rapid extension of the transmitted rays; the meta-compound also shows a weak, shallow band 1/λ 4110 (λ 2430), and the para-compound shows a wide, fairly strong band at 1/λ 3800 (λ 2630).

o-*Nitrobenzaldehyde.*—The absorption spectrum of the vapour of the substance at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure in mm. | |
|---|---|---|
| 90 | 922 | The rays were moderately well absorbed between about λ 2540—λ 2330, and then weakly transmitted to about λ 2260. |
| 100 | 938 | The rays were transmitted to about λ 2580. |

There was therefore a very weak vapour band, not unlike the solution band, except that the latter is shifted more towards the red end. Also, the fine series of vapour bands, found in the vapour of benzaldehyde, have completely disappeared.

FIG. 3.



I. o-*Nitrobenzaldehyde* (dash and dot line).
II. m-*Nitrobenzaldehyde* (dash and two dots line).
III. p-*Nitrobenzaldehyde* (continuous line).
IV. o-*Nitroaniline* (dash and cross).

m-*Nitrobenzaldehyde.*—The absorption spectrum of the vapour of the substance at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure in mm. | |
|---|---|---|
| 75 | 900 | The rays were transmitted to about λ 2260; but they were a little weak between λ 2450—λ 2350. |
| 100 | 947 | The rays were transmitted to about λ 2510. |

There was therefore an exceedingly weak band, which is comparable with the very shallow solution band.

p-*Nitrobenzaldehyde.*—The absorption spectrum of the vapour of the substance at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure in mm. | |
|---|---|---|
| 90 | 930 | The rays were absorbed between λ 2580—λ 2321, and then weakly transmitted to about λ 2144. |
| 100 | 947 | The rays were transmitted to λ 2650, but the Cd lines 2194 and 2144 were visible. |

There was therefore a fairly strong, wide band, which is comparable with the solution band, except in position.

*Nitromethane.*—Baly and Desch (T., 1908, **93**, 1747) state that solutions of the substance exhibit a shallow band the head of which is at about 1/λ 3600 (λ 2776).

The absorption spectrum of the vapour of nitromethane at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

| t°. | Pressure in mm. | |
|---|---|---|
| 45 | 843 | The rays were transmitted to λ 2360; but they appeared to be a little weak between about λ 2850—λ 2670. |
| 60 | 873 | The rays were transmitted to λ 2960: but the strong Cd lines 2880, 2748, 2573 were visible. |
| 90 | 933 | The rays were transmitted to about λ 3100. |

There was, therefore, the doubtful appearance of a very weak vapour band which would be comparable with the shallow solution band, but there was no appearance of a series of fine bands. It will be noticed that the vapour absorbs the light very strongly at the higher temperatures and pressures.

### *Thin Films.*

Thin films of several of the substances were also investigated by pressing tightly a small quantity of the substance between two quartz plates held in front of the slit of the spectroscope, and allowing the light of a cadmium spark to pass through for various periods of times. There was no solidification of the solids during the time of the experiment. The following phenomena were observed when the cadmium light passed through the thin films of the substances for two minutes:

| | |
|---|---|
| *Phenol*...... | The rays were absorbed between about λ 2850—λ 2540 and were then transmitted to λ 2330. |
| o-*Cresol* ... | The rays were absorbed between about λ 2870—λ 2570 and were then transmitted to λ 2350. |
| m-*Cresol* ... | The rays were absorbed between λ 2850—λ 2580 and were then transmitted to λ 2350. |
| p-*Cresol* ... | The rays were absorbed between λ 2920—λ 2580 and were then transmitted to λ 2360. |
| *Catechol* ... | The rays were absorbed between λ 2880—λ 2570 and then transmitted to about λ 2350: but the series of Cd lines from λ 2329 to λ 2265 were visible. |
| *Guaiacol* ... | The rays were absorbed between λ 2890—λ 2580 and then transmitted to λ 2400. |

*Nitrobenzene.*—The absorptive power of this substance is very great. It was only by very tightly squeezing the thinnest film that the light in the regions beyond about λ 3200 left an image on the photographic plate. After five minutes' exposure, the plate showed that the rays were transmitted very feebly to about λ 2480; there was then absorption to the cadmium line λ 2329, and then the series of cadmium lines to λ 2144 were fairly well seen.

Therefore the absorption bands are similar to the solution bands. There is no appearance of any of the fine vapour bands, and the results are precisely similar to those found in all cases of thin films of the various substances in previous investigations.

Some reference should be made to the divergences noticed by Baly and Rice (T., 1913, **103**, 91) in the observations of the absorption spectrum of thin films of aniline as described before (Purvis, *loc. cit.*). They suggest that the mounting of the quartz plates in the cell was not sufficiently rigid to stand the strain of the surface tension of such thin films; and that therefore the readings are much smaller than the real thickness of the film owing to the plates being forced apart by the surface tension. The authors have repeated the experiments with a film of aniline at 0·01 mm. thick, and found very similar results to what one of them found before, when using the same apparatus and the cadmium spark as the source of light. It is hardly likely that the divergences are caused by a weak rigidity of the quartz plates. Moreover, it is desirable that the exact conditions of the experimental apparatus should be stated; for example, the nature and size of the electric coil and the condenser will produce differences in the luminosity of the spark. The nature of the electrodes producing the spark, the distance of the latter from the slit, and the time of exposure will all affect the amount of light endeavouring to pass through; and in all quantitative and comparative experiments it seems to be necessary that all these conditions should be stated. With regard to the films of about 0·001 mm. thick, it was stated at the time that no great degree of exactness could be ascribed to the number. Such a thin film is difficult to obtain, for it implies plane surfaces of the quartz plates only obtainable by special methods.

### *Discussion of the Results.*

The more important results are: (1) The large number of vapour bands in phenol quite unlike the single solution band. (2) The reduction of the number of vapour bands in catechol and guaiacol. (3) The reduction of the number of vapour bands in the cresols, but not to the same extent as in the dihydroxy-compounds. (4) The reduction of the number of vapour bands in the chlorophenols, but not to the same extent as in the cresols. (5) The reduction of the number of vapour bands in the chloroanilines when compared with those found in the vapour of aniline. (6) The reduction of the number of vapour bands in benzophenone and acetophenone when compared with the vapour of benzaldehyde. (7) The total obliteration of the finer vapour bands in the nitro-derivatives of benzene, the toluenes, the phenols, the anilines, and the aldehydes; and the similarity of the vapour bands with the solution bands, except that the latter are shifted more towards the less refrangible regions. (8) Of the isomeric substances, the ortho-compound is the most disturbed and in the meta- and para-compounds it is sometimes the former and sometimes the latter which resembles the parent substance most closely; for example, attention may be called to the cresols and the chlorophenols as illustrations.

In previous communications (Purvis, T., 1910, **97**, 692, 1035, 1546; 1911, **99**, 811, 1699, 2318) the absorption spectra of the vapours of various organic substances were discussed from the view that the fundamental vibrations were considered to be damped and dislocated by the introduction of various substituting atoms or groups of atoms; that, in solution, the tensional forces at the surfaces of the two substances restrain the oscillations still more strongly; and that the solvent also acts as an absorbent of a part of the radiant energy as well as a barrier to the mutual encounters; and that, in the thin films of the substance, the closely-packed molecules also exert a tensional effect on each other, and thereby restrict the oscillatory movements. It was also suggested that the final adjustment of the oscillations would be influenced by the mass and type of the introduced atom or atomic groups, as well as by the distribution and reaction of the vibrations consequent on the absorption of the radiant energy. For example, none of the iodine derivatives of benzene or toluene (*loc. cit.*) shows any selective absorption either as vapour or in solution or in thin films, whereas the corresponding chlorine and bromine compounds show selective absorption. It was considered that the radiant energy is primarily exerted on the movements of the molecules themselves producing general absorption; and that therefore there are no oscillations or vibrations of the atoms which could produce selective absorption in the ultra-violet regions.

In later investigations the authors (T., 1912, **101**, 1514, 1810; this vol., p. 433) have amplified these suggestions, and they summitted that selective absorption may arise from the interaction of various primary oscillation centres, such as the carbonyl group, and the ethenoid linking. In order to extend this theory further, it is suggested that the oscillation centres are centres of electronic vibrations, set in motion by and so absorbing selectively part of the radiant energy; but the fuller development of the suggestion must be deferred until a more precise discussion can be brought forward to explain the complex phenomena in these compounds.

We desire to thank the Government Grant Committee of the Royal Society, by whose assistance a part of the cost of the research was defrayed.

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## CXVIII.—*Viscosity Maxima and Their Interpretation.*

By FERDINAND BERNARD THOLE, ALBERT GEORGE MUSSELL, and ALBERT ERNEST DUNSTAN.

SOME years ago (T., 1904, **85**, 817; 1905, **87**, 11) one of the present authors determined the viscosity-concentration curves of several liquid mixtures, and classified them as follows:

1. Sagged curves approximating more or less to the linear curve demanded by the law of mixtures.
2. Curves exhibiting a minimum.
3. Curves possessing a maximum.

Based on the view that associated liquids in general, and hydroxylated liquids in particular have a relatively high viscosity coefficient, the conclusion was drawn that a maximum point in a viscosity-concentration curve meant further association proceeding in the direction of complex formation, whilst the existence of a minimum point tended to the opposite view, namely, that some dissociation had resulted.

In the meantime several investigators have approached the problem, and in general the above deductions have been substantiated.

As a complete collection of viscosity curves which show a maximum point is given in the sequel, mention will only be made here very briefly of the conclusions which have been arrived at. The simple view taken by Graham (*Phil. Trans.*, 1861, **151**, 373) that the maximum point definitely indicated the existence of a compound, and, moreover, established its composition has been generally criticised as being far too explicit. It seems probable, however, that in some cases this view is sound, as will be seen later. Where, however, the amount of chemical affinity between the components is not sufficient entirely to bring about combination, the position of the maximum will vary within limits depending on temperature, the viscosity of the constituent liquids, and the degree of dissociation of the compound.

Washburn (*Tech. Quart.*, 1908, **21**, 399), in a valuable summary of the theory of hydration, dealing with the deviations of property-composition curves from those demanded by the law of mixtures, agrees that striking irregularities exist, which may be quite invariant with temperature, such as the expansion-coefficient of aqueous solutions of nitric acid and sulphuric acid, which clearly indicate the existence of the hydrates $HNO_3,H_2O$; $H_2SO_4,H_2O$. Such irregularities are not found for mixtures the components of which show no chemical affinity for each other. However, Washburn sums up his review by stating that the deviations of a physical property from the mixture law cannot give any conclusive evidence regarding the existence of a hydrate (or complex). This statement is directly contrary to the views which have been held by a great number of investigators in this field (see T., 1909, **95**, 1556).

Tsakalotos (*Bull. Soc. chim.*, 1908, [iv], **3**, 234) has also determined maximum points on viscosity-concentration curves, and holds the opinion that the study of the viscosity curves in conjunction with the freezing-point curves proves undoubtedly that the viscosity maxima must be attributed to molecular compounds in a state of partial dissociation. The discrepancy between the compositions of the mixtures of maximum viscosity and maximum freezing point for aniline–*m*-cresol, *p*-toluidine–*m*-cresol must be attributed to the difference existing between the viscosity of the two components and the partial dissociation of the molecular aggregate. He imagines the mixture as containing two different components, namely, (1) the inactive mixture of the original constituents, and (2) the complex aniline–phenol. Mixture (1) gives a linear mixture-law curve. The effect of (2) alone would be a maximum at 50 mols. per cent. The resultant of these curves has a maximum displaced towards the component of greater viscosity.

Faust (*Zeitsch. physikal. Chem.*, 1912, **95**, 1557) points out that it is very probable, although not absolutely proved, that in those cases where a maximum viscosity occurs a chemical compound is produced. Thus there is always such a maximum when the components are an acid and a base. In all cases where there is an evolution of heat on mixing, the compounds will dissociate with rising temperature, and so the viscosity curve will reproduce the dissociation by showing a smaller and smaller deviation, and at high temperatures will approach linearity. It is, however, untrustworthy to deduce from the position of the maximum the chemical composition of the compound, since the position frequently alters with temperature, and depends on the relative viscosities of the two components. On the other hand, when the viscosity curve is sagged, it must be interpreted as a result of dissociation (see Dunstan, T., 1904, *loc. cit.*). Faust also noticed that maxima on viscosity curves correspond with minima on vapour-pressure curves, a fact which is compatible with the formation of a molecular compound.

Denison (*Trans. Faraday Soc.*, 1912, **8**, 20) considers that the formation of a maximum does imply molecular aggregation, but prefers to determine the nature of the complex by the maximum deviation from the mixture law rather than from the position of the maximum itself. It should be mentioned that other observers have emphasised the fact that the greatest deviation should be considered, and not the actual maximum, notably Findlay (*Zeitsch. physikal. Chem.*, 1909, **69**, 203). Denison assumes that where complex formation is possible, there will be a solution of the complex in a mixture of the unaltered components. This mixture of complex and unchanged components will tend to form a maximum at some point along the curve, depending on its relative viscosity. It follows as a corollary that if most or all of the components associate in this way, the maximum point must agree with the composition of the complex. As Baker (T., 1912, **101**, 1416) has indicated, however, the complex may be of less viscosity than one or other of the components (assumed to be very associated), in which case a sagged curve or a minimum might be obtained. Baker, in fact, draws the conclusion that in mixtures of alcohol–ether, used for dissolving nitrocellulose, there is a complex existing, but the shape of the curve does not in any way indicate it.

Kendall (*Medd. K. Vetensk. Nobelinst.*, 1913, **2**, No. 25), dealing with liquid mixtures of type 1, shows that the viscosity found agrees excellently with that calculated on a modified Arrhenius formula, and hence strengthens the view that in such mixtures there is little mutual action.

On surveying these various opinions, it will be evident that they conform to the belief that a maximum viscosity does indicate some molecular aggregation, but the mass of evidence is decidedly against any predication that the position of the maximum point may indicate the composition of the compound. It will be obvious that this position can be influenced by a variety of causes. Suppose two liquids, $A$ and $B$, the association factors of which are $n$ and $m$, tend on mixing to form the compound $AB$. Then:

$$A_n + B_m \rightleftharpoons (n-x)A + (m-x)B + xAB,$$

where $x$ is the amount of $AB$ present.

Four cases present themselves:

*Case* 1.—$x$ is very small, and $A_n$ and $B_m$ are stable, and have little mutual action. A linear or slightly sagged curve will result, for example, phenol—α-naphthylamine.

*Case* 2.—$x$ is fairly large, there is considerable chemical affinity, and the complexes $A_n$ and $B_m$ are mutually fairly stable. Then if the viscosity of the complex $AB$ is less than that of one or other of the components, there will be a sagged curve, for example, phenol–acetone, lactic acid–water.

*Case* 3.—$x$ is fairly large, there is considerable chemical affinity, and the viscosity of the complex is greater than that of $A_n$ and $B_m$, which are mutually somewhat unstable. Then there will be a maximum point, but its position will depend on temperature and the relative viscosities of $A_n$, $B_m$, and $AB$, for example, alcohol–water.

*Case* 4.—$x$ is very large, and chemical action very considerable; the complexes $A_n$ and $B_m$ are dissociated. Then there will be a definite maximum corresponding with the actual molecular concentration of $A$ and $B$ in $AB$, for example, sulphuric acid–water.

In view of these considerations, we decided to investigate other cases of possible maximum formation, using pairs of liquids the fusion curves of which had been constructed, and we find, in brief, that in the large majority of cases a maximum in the melting-point curve means a maximum in the viscosity curve. We have found only one case as an exception to this rule, namely, acetone–phenol (Schmidlin and Lang, *Ber.*, 1910, **43**, 2812), which shows the existence of a compound at the fusion temperature, but gives only a very sagged viscosity curve. It should be mentioned also that the maximum viscosity for acetic acid–water does not correspond with a maximum in the fusion curve, apparently only a eutectic point being obtained.

*Liquid Mixtures which show Maximum Points.*

| Mixture. | Maximum. | Observer. | Fusion curve. |
|---|---|---|---|
| Water–methyl alcohol | Approximately $MeOH,3H_2O$ | Getman. Dunstan | — |
| Water–ethyl alcohol | Approximately $EtOH,3H_2O$ | Poisseule, Graham, Dunstan, Traube | — |
| Water–propyl alcohol | Approximately $PrOH,2H_2O$ | Dunstan | |
| Water–acetic acid | $CH_3{\cdot}CO_2H,H_2O$ | Graham, Dunstan, Wijkander | No maximum, Kremann, *Sitzungsber. K. Akad. Wien*, 1907, **116**, 795 |
| Water–propionic acid | Approximately, $C_2H_5{\cdot}CO_2H,H_2O$ | Tsakalotos | |
| Water–pyridine | Approximately $2C_5H_5N,5H_2O$ | Hartley, Thomas and Applebey | |
| | Approximately 30 mols. per cent. pyridine | Dunstan and Faust | |

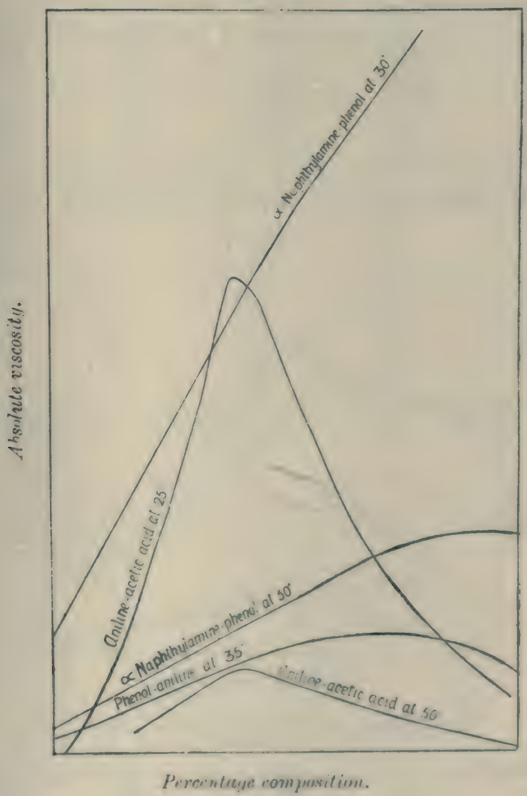
*Liquid Mixtures which show Maximum Points* (continued).

| Mixture. | Maximum. | Observer. | Fusion curve. |
|---|---|---|---|
| Water–sulphuric acid | $H_2SO_4,H_2O$ | Graham, Knietsch, Dunstan | Maximum, $H_2SO_4,H_2O$, Knietsch, Kremann |
| Sulphuric acid–sulphur trioxide | $H_2SO_4,SO_3$ | Dunstan and Wilson | Knietsch, maximum |
| Aniline–*m*-cresol | Approximately 2 *m*-cresol : 1 aniline | Tsakalotos | Maximum, Kremann, *Sitzungsber. K. Akad. Wien*, 1905, **112**, 1201. |
| *o*-Toluidine–*m*-cresol | Approximately 4 *m*-cresol : 1 toluidine | Tsakalotos | Kremann, *loc. cit.* |
| Acetone–chloroform. | Approximately 4 chloroform : 1 acetone at 0° | Tsakalotos | |
| | and 3 chloroform : 1 acetone at 13° | Faust | |
| | No maximum at 19° | Faust | |
| Pyridine–acetic acid | Approximately 4 acetic acid : 1 pyridine | Tsakalotos | |
| | Approximately 4 acetic acid : 1 pyridine | Faust | |
| | Very slight shift of maximum between 0° and 99° | Faust | |
| Pyridine–butyric acid | Approximately 4 butyric acid : 1 pyridine | Tsakalotos | |
| Aniline–acetic acid. | Approximately 2 acetic acid : 1 aniline at 18°—60° | Faust | |
| Acetic anhydride–water | Approximately 2 water : 1 anhydride, invariant between 0° and 73° | Faust | |
| *iso*Butyric acid–water | Approximately 3 water : 1 acid | Tsakalotos | |
| *n*-Butyric acid–water | Approximately 2 water : 1 acid | Tsakalotos | |
| Triethylamine–water | Approximately 5 water : 1 amine | Tsakalotos | |
| Nicotine–water | Approximately 3 water : 1 amine | Tsakalotos | |
| Allylthiocarbimide–piperidine | Exactly 1 amine : 1 thiocarbamide | Kurnakov and Schemtschushni, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1964 | |
| Phenylthiocarbimide–diethylamine | Exactly 1 amine : 1 thiocarbamide | ,, | |
| Allylthiocarbimide–methylaniline | Exactly 1 amine : 1 thiocarbamide | ,, | |
| Ethylthiocarbimide–piperidine | Exactly 1 amine : 1 thiocarbamide | ,, | |

## EXPERIMENTAL.

We have examined the following liquid pairs: Aniline–acetic acid, *o*-chlorophenol–aniline, *p*-chlorophenol–aniline, *m*-chlorophenol–aniline, phenol–phenylhydrazine, *o*-chlorophenol–phenylhydrazine, *p*-cresol–aniline, *p*-toluidine–phenol, α-naphthylamine–phenol, aniline–phenol, *o*-nitrophenol–*p*-toluidine, and phenol–diphenylamine.

FIG. 1.



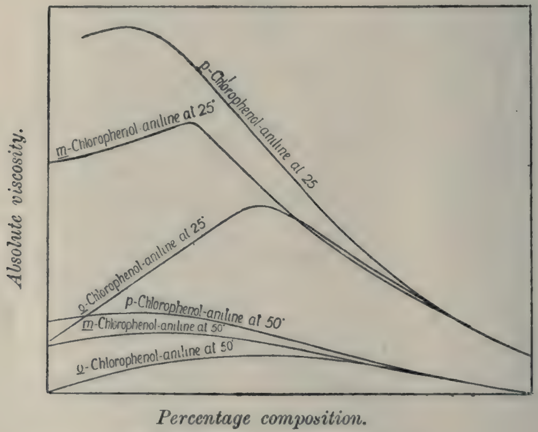
The materials used were obtained from Schuchardt, and carefully purified by appropriate means. The apparatus used has been fully described in the past, but mention may be made of the new type of Ostwald viscometer described recently by one of us (Thole, this vol., p. 22), which seems absolutely free from the drawbacks inherent to the vertical type. In several cases we have determined the viscosity at two temperatures to decide whether an appreciable drift of maximum does occur. It may be said at once that where there is any considerable amount of affinity between the components no such drift is noticeable.

### 1. *Aniline–Acetic Acid.* (Fig. 1.)

| Aniline, Per cent. | $d_{25°}$ | $\eta_{25°}$ | $d_{50°}$ | $\eta_{50°}$ |
|---|---|---|---|---|
| 0·0 | 1·052 | 0·0134 | — | — |
| 15·5 | 1·082 | 0·0729 | 1·047 | 0·0296 |
| 24·7 | 1·091 | 0·123 | — | — |
| 37·9 | 1·088 | 0·219 | 1·056 | 0·0565 |
| 40·9 | 1·085 | 0·214 | 1·057 | 0·0558 |
| 44·5 | 1·084 | 0·203 | 1·051 | 0·0523 |
| 49·55 | 1·076 | 0·181 | — | — |
| 62·3 | 1·061 | 0·118 | 1·035 | 0·0382 |
| 100·0 | 1·022 | 0·0362 | 0·992 | 0·0201 |

Maximum at 25°, 40 per cent. aniline; at 50°, 39 per cent. $C_6H_5·NH_2,CH_3·CO_2H$ requires 61 per cent. aniline.

FIG. 2.



### 2. *Aniline–o-Chlorophenol.* (Fig. 2.)

| Aniline. Per cent. | $d_{25°}$ | $\eta_{25°}$ | $d_{50°}$ | $\eta_{50°}$ |
|---|---|---|---|---|
| 0·0 | 1·235 | 0·0411 | 1·203 | 0·02015 |
| 8·4 | 1·216 | 0·0538 | 1·184 | 0·0257 |
| 15·9 | 1·199 | 0·0671 | 1·168 | 0·0288 |
| 40·4 | 1·146 | 0·0951 | 1·118 | 0·0330 |
| 41·8 | 1·142 | 0·0963 | 1·114 | 0·0335 |
| 49·95 | 1·134 | 0·0944 | 1·105 | 0·0326 |
| 61·4 | 1·099 | 0·0771 | 1·072 | 0·0304 |
| 70·3 | 1·079 | 0·0649 | 1·053 | 0·0287 |
| 100·0 | 1·022 | 0·0362 | 0·992 | 0·0201 |

Maximum at 25°, 45 per cent. aniline. Maximum at 50°, 44 per cent. aniline.

$C_6H_5·NH_2,C_6H_4Cl·OH$ requires 42 per cent. aniline.

### 3. *Aniline–*m*-Chlorophenol.* (Fig. 2.)

| Aniline. Per cent. | $d_{25}$. | $\eta_{25}$. | $d_{50}$. | $\eta_{50}$. |
|---|---|---|---|---|
| 0·0 | 1·268 | 0·1155 | 1·237 | 0·0398 |
| 9·0 | 1·238 | 0·1185 | 1·210 | 0·04135 |
| 19·35 | 1·207 | 0·1246 | 1·180 | 0·0434 |
| 30·1 | 1·181 | 0·1322 | 1·153 | 0·0449 |
| 40·3 | 1·153 | 0·1083 | 1·126 | 0·0403 |
| 60·1 | 1·104 | 0·0811 | 1·077 | 0·0321 |
| 75·4 | 1·071 | 0·0613 | 1·045 | 0·0265 |
| 100·0 | 1·022 | 0·0362 | 0·992 | 0·0210 |

Maximum at 25°, 29 per cent. Maximum at 50°, 29 per cent.

$C_6H_5{\cdot}NH_2,C_6H_4Cl{\cdot}OH$ requires 42 per cent. aniline.

### 4. *Aniline–*p*-Chlorophenol.* (Fig. 2.)

| Aniline. Per cent. | $d_{25}$. | $\eta_{25}$. | $d_{50}$. | $\eta_{50}$. |
|---|---|---|---|---|
| 0·0 | — | — | 1·244 | 0·0499 |
| 7·8 | 1·249 | 0·168 | 1·223 | 0·0514 |
| 15·4 | 1·228 | 0·172 | 1·199 | 0·0537 |
| 22·2 | 1·209 | 0·171 | 1·179 | 0·0537 |
| 29·9 | 1·185 | 0·157 | 1·158 | 0·0513 |
| 37·2 | 1·166 | 0·141 | 1·140 | 0·0480 |
| 41·8 | 1·154 | 0·131 | 1·128 | 0·0451 |
| 50·2 | 1·133 | 0·112 | 1·107 | 0·0419 |
| 70·2 | 1·084 | 0·0705 | 1·058 | 0·0307 |
| 90·3 | 1·037 | 0·0452 | 1·012 | 0·0221 |
| 100·0 | 1·022 | 0·0362 | 0·992 | 0·0201 |

Maximum at 20 per cent. aniline. Maximum at 20 per cent. aniline.

$C_6H_5{\cdot}NH_2,C_6H_4Cl{\cdot}OH$ requires 42 per cent. aniline.

### 5. *Phenylhydrazine–Phenol.* (Fig. 3.)

Maximum in fusion curve at equimolecular proportions (Ciusa and Bernardi, *Gazzetta*, 1910, **40**, i, 159).

| Phenyl hydrazine. Per cent. | $d_{50}$. | $\eta_{50}$. | Phenyl hydrazine. Per cent. | $d_{50}$. | $\eta_{50}$. |
|---|---|---|---|---|---|
| 0·0 | 1·048 | 0·0320 | 53·7 | 1·069 | 0·0820 |
| 20·2 | 1·056 | 0 0525 | 62·8 | 1·069 | 0·0805 |
| 40·2 | 1·065 | 0·07485 | 80·4 | 1·069 | 0·06555 |
| 50·1 | 1·068 | 0·0802 | 100 0 | 1·068 | 0·0458 |

Maximum at 54 per cent. phenylhydrazine.

$NHPh{\cdot}NH_2,PhOH$ requires 53 per cent. phenylhydrazine.

### 6. *Phenylhydrazine–*o*-Chlorophenol.* (Fig. 3.)

| Phenyl hydrazine. Per cent. | $d_{50}$. | $\eta_{50}$. | Phenyl hydrazine. Per cent. | $d_{50}$. | $\eta_{50}$. |
|---|---|---|---|---|---|
| 0·0 | 1·203 | 0 02015 | 49·3 | 1·145 | 0·0818 |
| 14·75 | 1·187 | 0·0351 | 75·0 | 1·108 | 0·06955 |
| 36·0 | 1·166 | 0·0716 | 100·0 | 1·068 | 0·0458 |
| 46·5 | 1·154 | 0·0827 | | | |

Maximum at 46 per cent. phenylhydrazine.

$NHPh{\cdot}NH_2,C_6H_4Cl{\cdot}OH$ requires 46 per cent. phenylhydrazine.

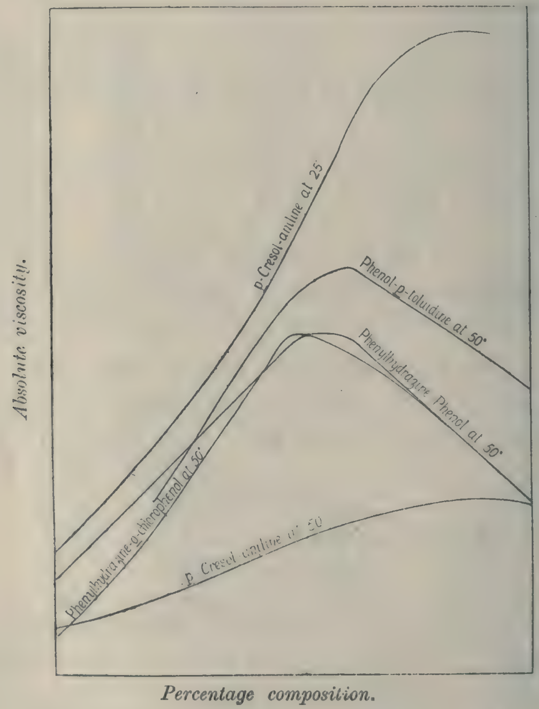
### 7. p-*Cresol–Aniline*. (Fig. 3.)

| *p*-Cresol. Per cent. | $d_{25}$. | $\eta_{25}$. | $d_{50}$. | $\eta_{50}$. |
|---|---|---|---|---|
| 0·0 | 1·020 | 0·0362 | 0·992 | 0·0201 |
| 30·0 | 1·022 | 0·0695 | 0·997 | 0·0293 |
| 53·6 | 1·027 | 0·107 | 1·001 | 0·03975 |
| 62·7 | 1·028 | 0·124 | 1·004 | 0·0426 |
| 79·5 | 1·028 | 0·144 | 1·005 | 0·0462 |
| 90·0 | 1·029 | 0·145 | 1·005 | 0·0471 |
| 100·0 | — | — | 1·005 | 0·0462 |

Maximum at 25°, 86 per cent. *p*-cresol. Maximum at 50°, 90 per cent. *p*-cresol.

Maximum on fusion curve at equimolecular proportions (Philip, T., 1903, **83**, 814).

FIG. 3.



### 8. *Phenol*–p-*Toluidine*. (Fig. 3.)

| Phenol. Per cent. | $d_{30}$. | $\eta_{30}$. |
|---|---|---|
| 0·0 | — | — |
| 39·9 | 1·016 | 0·0757 |
| 47·5 | 1·021 | 0·0864 |
| 58·8 | 1·032 | 0·0942 |
| 62·2 | 1·0375 | 0·0962 |
| 71·5 | 1·043 | 0·0894 |
| 100·0 | 1·067 | 0·0700 |

Maximum at 63 per cent. phenol.

$PhOH,C_6H_4Me\cdot NH_2$ requires 48 per cent. phenol.

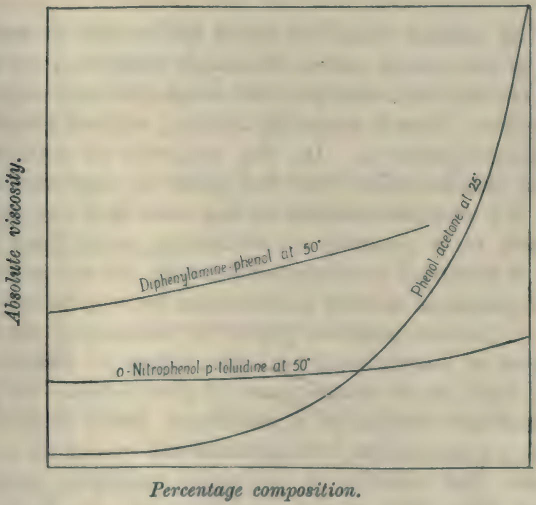
Maximum on fusion curve at equimolecular proportions (Philip)

### 9. *α-Naphthylamine–Phenol.* (Fig. 1.)

| α-Naphthylamine. Per cent. | $d_{30}$. | $\eta_{30}$. | $d_{50}$. | $\eta_{50}$. |
|---|---|---|---|---|
| 0·0 | 1·067 | 0·0700 | 1·048 | 0·0320 |
| 52·0 | 1·094 | 0·249 | 1·075 | 0·0852 |
| 56·5 | 1·097 | 0·269 | 1·076 | 0·0900 |
| 79·1 | 1·106 | 0·324 | 1·092 | 0·109 |
| 92·5 | — | — | 1·102 | 0·113 |
| 100·0 | — | — | 1·108 | 0·112 |

Maximum at 50°, 92 per cent. α-naphthylamine.
Maximum on fusion curve at equimolecular proportions (Philip).

FIG. 4.



### 10. *Aniline–Phenol.* (Fig. 1.)

| Phenol. Per cent. | $d_{35}$. | $\eta_{35}$. |
|---|---|---|
| 0·0 | 1·007 | 0·0279 |
| 35·1 | 1·030 | 0·0539 |
| 51·4 | 1·040 | 0·0654 |
| 67·9 | 1·049 | 0·0721 |
| 79·7 | 1·055 | 0·0692 |
| 100·0 | — | 0·0555 |

Maximum at 70 per cent. phenol.

Maximum on fusion curve at equimolecular proportions (Schreinemakers, *Zeitsch. physikal. Chem.*, 1899, **31**, 581).

### 11. *Diphenylamine–Phenol.* (Fig. 4.)

| Diphenylamine. Per cent. | $d_{50}$. | $\eta_{50}$. |
|---|---|---|
| 0·0 | 1·048 | 0·0320 |
| 32·4 | 1·048 | 0·03825 |
| 58·9 | 1·052 | 0·04362 |
| 79·5 | 1·055 | 0·0501 |
| 100·0 | — | — |

A very slightly sagged curve. Philip showed (*loc. cit.*) that the fusion curve only exhibits a eutectic point.

### 12. o-*Nitrophenol*–p-*Toluidine*. (Fig. 4.)

| *o*-Nitrophenol. Per cent. | $d_{50^{\circ}}$ | $\eta_{50^{\circ}}$ |
|---|---|---|
| 0·0 | 0·958 | 0·0180 |
| 35·3 | 1·050 | 0·01835 |
| 79·6 | 1·220 | 0·0215 |
| 100·0 | 1·282 | 0·0268 |

A distinctly sagged curve. Philip showed also that this system merely gave a eutectic point.

It will be noticed from the above tables that in some cases the evidence of the fusion curves is closely paralleled by that of the viscosity curves, for example, for sulphuric acid–water, *o*-chlorophenol–aniline, phenol–phenylhydrazine, aniline–phenol, *o*-chlorophenol–phenylhydrazine. In the majority of maxima, however, there is a distinct shift from the point of equimolecular concentration. We therefore incline to the view that the appearance of a maximum on a viscosity concentration curve does indicate the existence of chemical combination between the components, but the position depends on several independent factors, namely, the actual viscosity of the components (which is intimately connected with their degree of association), and the degree of dissociation of the compound itself at the temperature of observation. It by no means follows that the absence of a maximum point precludes complex formation, as, indeed, has been pointed out by one of us repeatedly, for obviously the viscosity of one highly associated component may be greater than that of the complex (see also Baker, *loc. cit.*). Comparison of the viscosity with the fusion curves and with the vapour pressure curves is valuable, for, as Faust has indicated, there is a close connexion between vapour pressure and viscosity, since whatever forces operate in complex building would similarly depress vapour tension. In an attempt to test these views experimentally, we first determined the viscosity of two pairs, which gave only eutectic points on their fusion curves, namely, phenol–diphenylamine, and *o*-toluidine–*o*-nitrophenol (Philip, *loc. cit.*). We obtained a linear density curve and sagged viscosity curves (Fig. 4), which evidently confirms the view that little or no complex formation is proceeding, or else that the compound had a smaller viscosity than the components, but seeing that *o*-nitrophenol is very slightly associated (Thole, T., 1910, **97**, 2596), and its viscosity is depressed by adding phenol, it is obvious that no compound formation is going on. This is a case where Denison would probably suggest that the maximum sag was due to the appearance of a compound. Similar remarks may be made about the phenol–diphenylamine curve, which is almost linear.

It can therefore safely be predicted that wherever the two components show little tendency for chemical union a sagged curve, or one departing but slightly from linearity, will be found.

A very striking confirmation of the validity of these views has just appeared in a paper by Kurnakov and Schemtschushni (*loc. cit.*). These authors have investigated at various temperatures the viscosity concentration curves of irreversible binary systems where liquid and completely miscible compounds are formed. The viscosity isotherms consist of two separate branches convex to the composition axis intersecting at an angle (increasing in acuteness as the temperature is lowered), and this maximum point is invariant at exactly equimolecular concentration. This condition of affairs was predicted in Case 4.

The authors desire to thank the Research Fund Committee of the Chemical Society for grants in aid of this work.

EAST HAM TECHNICAL COLLEGE.

# CXIX.—*Preparation of Secondary Amines from Carboxylic Acids. Part III. Disecondary Amines from Dicarboxylic Acids.*

By HENRY RONDEL LE SUEUR.

THE first and second parts of this investigation (T., 1910, **97**, 2433; 1911, **99**, 827) dealt with the preparation of the higher alkyl derivatives of aniline and α- and β-naphthylamine by the action of heat on the corresponding α-anilino- and α-naphthylamino-acids. Thus it was shown that a 70 per cent. yield of pentadecylaniline is readily obtained from α-anilinopalmitic acid:

$$C_{14}H_{29}\cdot CH(NHPh)\cdot CO_2H \longrightarrow C_{15}H_{31}\cdot NHPh + CO_2.$$

The present communication deals with the results of a similar investigation of the α-anilino- and α-1- and 2-naphthylamino-derivatives of dicarboxylic acids, and the results obtained show that the decomposition by heat of these substituted dicarboxylic acids is in every way similar to that undergone by the analogous derivatives of monocarboxylic acids. Thus, αη-dianilinoazelaic acid, when heated above its melting point, readily loses carbon dioxide, and *s*-diphenylheptamethylenediamine results:

$$CO_2H\cdot CH(NHPh)\cdot[CH_2]_5\cdot CH(NHPh)\cdot CO_2H \longrightarrow NHPh\cdot[CH_2]_7\cdot NHPh + 2CO_2.$$

The preparation of the dianilino- and dinaphthylamino-acids presents no great difficulty, and the yield of amine is generally a very satisfactory one. Thus, 19 grams of pure *s*-diphenylheptamethylenediamine were obtained from 33 grams of azelaic acid by the following reactions:

$$\begin{tikzcd}
CO_2H\cdot[CH_2]_7\cdot CO_2H \arrow[r, "PCl_5", "Br_2"'] & COCl\cdot CHBr\cdot[CH_2]_5\cdot CHBr\cdot COCl \arrow[r, "EtOH"] & {} \\
\text{Azelaic acid.} & & CO_2Et\cdot CHBr\cdot[CH_2]_5\cdot CHBr\cdot CO_2Et \arrow[d, "PhNH_2"] \\
CO_2H\cdot CH(NHPh)\cdot[CH_2]_5\cdot CH(NHPh)\cdot CO_2H \arrow[d, "heat"] & & CO_2Et\cdot CH(NHPh)\cdot[CH_2]_5\cdot CH(NHPh)\cdot CO_2Et \arrow[ll, "KOH"'] \\
NHPh\cdot[CH_2]_7\cdot NHPh & &
\end{tikzcd}$$

It is obvious that there is no possibility of the formation of tertiary amines by the decomposition of these *α*-substituted acids, and this circumstance renders the method now described for the preparation of secondary amines preferable to the one commonly employed, that is, the action of an alkyl iodide on a primary amine. Further acids are more easily obtained than any other class of organic compounds, whereas monoalkyl iodides, especially the higher ones, are, as a rule, difficult to prepare.

## EXPERIMENTAL.

### *Diphenyloctamethylenediamine*, $NHPh\cdot[CH_2]_8\cdot NHPh$.

*αθ-Dianilinosebacic acid*,

$$CO_2H\cdot CH(NHPh)\cdot[CH_2]_6\cdot CH(NHPh)\cdot CO_2H,$$

was prepared by the action of aniline on ethyl *αθ*-dibromosebacate and subsequent hydrolysis of the anilino-ester, as described in a former communication (T., 1910, **97**, 180). The finely powdered dianilinosebacic acid, in quantities of 10 grams, was placed in a small distillation flask, which was connected to a second distillation flask, and the latter joined to a pump. When the pressure had fallen to 25—30 mm., the acid was carefully heated until it was all melted, and on raising the temperature further, carbon dioxide was readily given off. The evolution of gas is liable to become unduly rapid if the heating is effected too rapidly. When no more gas was evolved, the temperature was raised further, and the product slowly distilled. The distillate, which weighed 5·7 grams and readily solidified on cooling, was spread on porous plate and crystallised from light petroleum. The yield of pure amine was 69 per cent. of the theoretical:

0·1506 gave 0·4500 $CO_2$ and 0·1264 $H_2O$. C = 81·49; H = 9·33.
0·1278 „ 10·6 c.c. $N_2$ (moist) at 19·5° and 760 mm. N = 9·49.
$C_{20}H_{28}N_2$ requires C = 81·08; H = 9·45; N = 9·45 per cent.

s-*Diphenyloctamethylenediamine* is readily soluble in ether, chloroform, benzene, or acetone, but sparingly so in cold alcohol or light petroleum, and crystallises from the latter solvent in stellar groups of stout needles, melting at 61°. When treated with nitrous acid, it yields a product which gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*, $NHPh\cdot[CH_2]_8\cdot NHPh,2HCl$, was readily obtained as a crystalline precipitate by adding concentrated hydrochloric acid to a warm alcoholic solution of the amine, and was purified by crystallisation from alcohol containing a little hydrochloric acid. It is insoluble in the common organic solvents except alcohol, in which it is sparingly soluble. It melts and decomposes at about 258°:

0·1413 gave 9·4 c.c. $N_2$ (moist) at 13° and 758 mm. N = 7·84.
$C_{20}H_{28}N_2,2HCl$ requires N = 7·58 per cent.

s-*Diacetyldiphenyloctamethylenediamine*, $NPhAc\cdot[CH_2]_8\cdot NPhAc$, was prepared by boiling the base with an excess of acetic anhydride, and was purified by crystallisation from light petroleum, from which it separates in thin, glistening plates, melting at 86—87°. The compound dissolves readily in the common organic solvents except light petroleum, in which it is sparingly soluble:

0·1318 gave 8·3 c.c. $N_2$ (moist) at 16·5° and 768 mm. N = 7·40.
$C_{24}H_{32}O_2N_2$ requires N = 7·37 per cent.

The *benzenesulphonyl* derivative, $SO_2Ph\cdot NPh\cdot[CH_2]_8\cdot NPh\cdot SO_2Ph$, was prepared by heating in boiling water for five hours a mixture of half a gram of the base and 2 grams of benzenesulphonyl chloride dissolved in 10 grams of dry pyridine. The resulting solution was poured on crushed ice, and the solid collected, dried, and crystallised from alcohol:

0·1852 gave 8·5 c.c. $N_2$ (moist) at 15° and 766 mm. N = 5·40.
$C_{32}H_{36}O_4N_2S_2$ requires N = 4·90 per cent.

s-*Dibenzenesulphonyldiphenyloctamethylenediamine* is insoluble in ether or light petroleum, dissolves readily in benzene, chloroform, or acetone, and crystallises from alcohol in needles melting at 121—122°.

### *Preparation of αθ-Di-2-naphthylaminosebacic Acid,* $CO_2H\cdot CH(NH\cdot C_{10}H_7)\cdot[CH_2]_6\cdot CH(NH\cdot C_{10}H_7)\cdot CO_2H$.

Ten grams of ethyl αθ-dibromosebacate and 17 grams of β-naphthylamine were heated together for nine hours in a flask immersed in boiling water. The product was first repeatedly digested with hot dilute hydrochloric acid, and then crystallised from a mixture of alcohol and ethyl acetate, from which it separates in crystalline nodules, melting at 132—134°:

0·2426 gave 11·2 c.c. $N_2$ (moist) at 14° and 754 mm. N = 5·39.

$C_{34}H_{40}O_4N_2$ requires N = 5·19 per cent.

*Ethyl αθ-di-2-naphthylaminosebacate,*

$CO_2Et\cdot CH(NH\cdot C_{10}H_7)\cdot[CH_2]_6\cdot CH(NH\cdot C_{10}H_7)\cdot CO_2Et$,

is insoluble in ether or light petroleum, is sparingly so in boiling alcohol or ethyl acetate, and readily soluble in cold chloroform. The hydrolysis of the above ester was effected by boiling it with an excess of 10 per cent. alcoholic solution of potassium hydroxide. The resulting solution was poured into excess of hot dilute hydrochloric acid, and the precipitated acid collected, well washed, and dried. Owing to the insolubility of this naphthylamino-acid, no suitable solvent could be found for its purification by crystallisation, consequently it was twice dissolved in a dilute solution of potassium hydroxide and reprecipitated by dilute hydrochloric acid, filtered, well washed, and dried.

*αθ-Di-2-naphthylaminosebacic acid* is insoluble in water and all the common organic solvents; it melts with decomposition and evolution of gas at 222—227°:

0·2274 gave 11·5 c.c. $N_2$ (moist) at 16° and 758 mm. N = 5·88.

$C_{30}H_{32}O_4N_2$ requires N = 5·79 per cent.

### s-*Di-2-naphthyloctamethylenediamine,* $C_{10}H_7\cdot NH\cdot[CH_2]_8\cdot NH\cdot C_{10}H_7$.

αθ-Di-2-naphthylaminosebacic acid in quantities of 10 grams was heated under a pressure of 30 mm., as described for the preparation of diphenyloctamethylenediamine (p. 1120), and when the evolution of carbon dioxide had ceased, the temperature was raised, and the product slowly distilled at 20 mm. pressure. The semi-solid distillate was spread on porous plate, and the solid crystallised from a mixture of alcohol and light petroleum. The isolation of the base is difficult, and this no doubt accounts in some measure for the low yield (15 per cent.) of pure base obtained:

0·1636 gave 10·0 c.c. $N_2$ (moist) at 13° and 746 mm. N = 7·09.

$C_{28}H_{32}N_2$ requires N = 7·07 per cent.

s-*Di-2-naphthyloctamethylenediamine* is readily soluble in chloroform or benzene, sparingly so in ether or alcohol in the cold, and separates from the latter solvent in small, lens-shaped crystals, melting at 100°. The product obtained by treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*, $C_{10}H_7 \cdot NH \cdot [CH_2]_8 \cdot NH \cdot C_{10}H_7, 2HCl$, was obtained as a crystalline precipitate by passing dry hydrogen chloride through a solution of the base in benzene, and was purified by crystallisation from methyl alcohol, in which it is sparingly soluble. It melts and decomposes at 244°:

0·1516 gave 7·7 c.c. $N_2$ (moist) at 14° and 760 mm. N = 5·97.
$C_{28}H_{32}N_2, 2HCl$ requires N = 5·97 per cent.

### *Preparation of* αθ-*Di*-1-*naphthylaminosebacic Acid*, $CO_2H \cdot CH(NH \cdot C_{10}H_7) \cdot [CH_2]_6 \cdot CH(NH \cdot C_{10}H_7) \cdot CO_2H$.

Forty grams of ethyl αθ-dibromosebacate and 68 grams of α-naphthylamine were heated together in a flask immersed in boiling water for fourteen hours, and the product worked up, as described for the preparation of the corresponding β-naphthylamino-compound (p. 1122):

0·2228 gave 10·2 c.c. $N_2$ (moist) at 17° and 748 mm. N = 5·23.
$C_{34}H_{40}O_4N_2$ requires N = 5·19 per cent.

*Ethyl* αθ-*di*-1-*naphthylaminosebacate*,
$CO_2Et \cdot CH(NH \cdot C_{10}H_7) \cdot [CH_2]_6 \cdot CH(NH \cdot C_{10}H_7) \cdot CO_2Et$,
is insoluble in ether or light petroleum in the cold, dissolves readily in benzene, acetone, or chloroform, and separates from its solution in alcohol in crystalline nodules, melting at 117—119°.

αθ-*Di*-1-*naphthylaminosebacic acid* was obtained by hydrolysis of the above ester as described for the preparation of the corresponding 2-naphthylamino-acid. As the acid separates with difficulty from its solutions in organic solvents, it was purified by repeated solution in dilute potassium hydroxide and reprecipitation by acid. It is insoluble in light petroleum, but dissolves readily in alcohol, acetone, chloroform, or benzene, and separates slowly from its concentrated solution in ethyl acetate in small, crystalline nodules, which melt and decompose at about 180°:

0·2230 gave 10·2 c.c. $N_2$ (moist) at 13° and 770 mm. N = 5·48.
$C_{30}H_{32}O_4N_2$ requires N = 5·78 per cent.

### s-*Di*-1-*naphthyloctamethylenediamine*, $C_{10}H_7 \cdot NH \cdot [CH_2]_8 \cdot NH \cdot C_{10}H_7$.

αθ-Di-1-naphthylaminosebacic acid in quantities of 5 grams was heated, and the products distilled as described for the preparation of di-2-naphthyloctamethylenediamine (p. 1122). The alcoholic solution of the distillate slowly deposited well-formed prisms of the base, which were separated, and crystallised from methyl alcohol:

0·1060 gave 6·6 c.c. $N_2$ (moist) at 22° and 766 mm. N = 7·11.

$C_{28}H_{32}N_2$ requires N = 7·07 per cent.

s-*Di*-1-*naphthyloctamethylenediamine* is readily soluble in ether, benzene, or chloroform, sparingly so in ethyl or methyl alcohol, and crystallises from the latter solvent in stellar groups of stout needles, melting at 91—92°. The product obtained by treating the base with nitrous acid gives Liebermann's reaction for nitrosoamines.

The yield of pure amine was less than that of the corresponding β-naphthyl derivative, and the explanation given to account for the low yield of the latter applies even more so in the case of the former, since derivatives of α-naphthylamine are generally more difficult to crystallise than the β-naphthylamine compounds.

### *Ethyl αη-Dibromoazelate*, $CO_2Et{\cdot}CHBr{\cdot}[CH_2]_5{\cdot}CHBr{\cdot}CO_2Et$.

Twenty grams of pure azelaic acid (m. p. 105°) were treated with 45 grams of phosphorus pentachloride, and 39 grams of bromine slowly added to the resulting acid chloride. The mixture was carefully heated on the water-bath, and when all the bromine had disappeared, the bromo-acid chloride was poured slowly into 100 c.c. of alcohol. The alcoholic solution, after remaining overnight, was heated on the water-bath for half-an-hour, then cooled and poured into a large volume of water, and the ester extracted with ether. The ethereal solution was dried, evaporated, and the residue fractionally distilled under diminished pressure.

*Ethyl αη-dibromoazelate* is a colourless, oily liquid, boiling at 238°/30 mm.:

0·2436 gave 0·2234 AgBr. Br = 39·1.

$C_{13}H_{22}O_4Br_2$ requires Br = 39·8 per cent.

### *αη-Dianilinoazelaic Acid*,

### $CO_2H{\cdot}CH(NHPh){\cdot}[CH_2]_5{\cdot}CH(NHPh){\cdot}CO_2H$.

Twenty-five grams of ethyl αη-dibromoazelate and 28 grams of recently distilled aniline were heated together in a flask immersed in boiling water for nine hours. The product was poured into excess of dilute potassium hydroxide, and the precipitated anilino-ester and aniline extracted with ether. The ethereal solution was washed, dried, and the residue left on evaporation of the ether was heated at 230°/90 mm. in order to remove the excess of aniline. The undistilled residue, consisting of anilino-ester, was hydrolysed by boiling with a 25 per cent. alcoholic solution of potassium hydroxide, and when the hydrolysis was complete the solution was diluted with water, the alchool removed by evaporation, and the anilino-acid precipitated by the addition of dilute hydrochloric acid. Care must be taken not to add any large excess of mineral acid, otherwise the anilino-acid will be redissolved. The precipitated acid was collected, dried, and crystallised from alcohol, when it was obtained in small, crystalline nodules, melting at 192—194°. It is insoluble in light petroleum, ethyl acetate, or acetone in the cold, sparingly so in boiling alcohol, and dissolves readily in dilute hydrochloric acid:

0·1550 gave 10·2 c.c. $N_2$ (moist) at 15° and 762 mm. $N=7·72$.

$C_{21}H_{26}O_4N_2$ requires $N=7·57$ per cent.

0·1906, dissolved in alcohol, required 10·0 c.c. *N*/10-NaOH for neutralisation, using phenolphthalein as indicator, whereas the same amount of the dibasic acid, $C_{21}H_{26}O_4N_2$, requires 10·3 c.c. *N*/10-NaOH.

### s-*Diphenylheptamethylenediamine*, NHPh·[$CH_2$]$_7$·NHPh.

αη-Dianilinoazelaic acid was heated in quantities of not more than 25 grams and under 20 mm. pressure, as described for the preparation of diphenyloctamethylenediamine (p. 1120), and when the evolution of carbon dioxide had ceased, the product was distilled slowly. The distillate readily solidified on cooling, and was crystallised from a mixture of methyl alcohol and ether, from which the amine separates out in thin plates, melting at 51—52°:

0·1616 gave 0·4760 $CO_2$ and 0·1322 $H_2O$. $C=80·34$; $H=9·09$.

0·1460 „ 12·3 c.c. $N_2$ (moist) at 17° and 766 mm. $N=9·86$.

$C_{19}H_{26}N_2$ requires $C=80·85$; $H=9·22$; $N=9·93$ per cent.

s-*Diphenylheptamethylenediamine* is readily soluble in dilute hydrochloric acid and the common organic solvents except light petroleum and methyl alcohol. The product obtained by treating the base with nitrous acid gives Liebermann's reaction for nitrosoamines.

The decomposition of the anilinoazelaic acid into diphenylheptamethylenediamine and carbon dioxide takes place quite smoothly, and the yield of base is very satisfactory (see introduction, p. 1120).

The *hydrochloride*, NHPh·[$CH_2$]$_7$·NHPh,2HCl, was readily obtained by dissolving the base in warm hydrochloric acid and evaporating the solution in a vacuum. It was purified by crystallisation from a mixture of alcohol and ether, from which it separates out in stellar groups of needles, melting at 193—194°. It is insoluble in the common organic solvents with the exception of hot alcohol, in which it dissolves readily. Its aqueous solution is strongly acid to litmus:

0·1750 gave 11·4 c.c. $N_2$ (moist) at 18° and 771 mm. N = 7·63.
$C_{19}H_{26}N_2,2HCl$ requires N = 7·88 per cent.

The *acetyl* derivative, NPhAc·$[CH_2]_7$·NPhAc, was obtained by boiling for one hour on the water-bath a mixture of 1 gram of the base and 2 grams each of acetyl chloride and acetic anhydride. The excess of the two reagents was removed by allowing the product to remain over a concentrated solution of potassium hydroxide in a vacuum, and the residue crystallised from light petroleum:

0·1710 gave 11·6 c.c. $N_2$ (moist) at 19·5° and 764 mm. N = 7·82.
$C_{23}H_{30}O_2N_2$ requires N = 7·65 per cent.

s-*Diacetyldiphenylheptamethylenediamine* is readily soluble in alcohol, benzene, or chloroform, moderately so in boiling ether or light petroleum, and separates from the latter solvent in clusters of stout needles, melting at 79—80°.

The *benzenesulphonyl* derivative, $SO_2$Ph·NPh·$[CH_2]_7$·NPh·$SO_2$Ph, was prepared by heating for five hours in boiling water a mixture of 1·5 grams of the base and 4 grams of benzenesulphonyl chloride dissolved in 14 c.c. of dry pyridine. The resulting solution was poured on crushed ice, the precipitated solid dissolved in ether, and the ethereal solution washed with dilute hydrochloric acid and water and dried. The residue left on evaporation of the ether was crystallised from alcohol:

0·1846 gave 8·4 c.c. $N_2$ (moist) at 15° and 766 mm. N = 5·37.
$C_{31}H_{34}O_4N_2S_2$ requires N = 4·98 per cent.

s-*Dibenzenesulphonyldiphenylheptamethylenediamine* is readily soluble in chloroform, benzene, or acetone, and crystallises from alcohol in stout prisms, melting at 96—97°.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant, which has, in part, defrayed the expenses of this investigation.

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# VAN'T HOFF MEMORIAL LECTURE.

Delivered on May 22nd, 1913,

By James Walker, D.Sc., Ph.D., LL.D., F.R.S.

The work of van't Hoff is indissolubly woven in the texture of the chemistry of to-day. Whether we are organic chemists, inorganic chemists, or physical chemists, we constantly utilise and apply his ideas, reap the benefit of the intense thought he devoted to the fundamental problems of our science. This is his splendid and enduring memorial. Nothing can add to it, nothing detract from it. Feeling this profoundly, I conceive that I may best discharge the honourable responsibility laid upon me by the Society if I give a sketch of his life, his main achievements, and his way of thinking with as little discussion and elaboration as possible, and as simply as I may.*

Jacobus Henricus van't Hoff was born in Rotterdam on the 30th of August, 1852. He came of pure Dutch stock, and his ancestry can be traced back to one Adriaen van't Hoff, who lived in the latter half of the seventeenth century at Groote Lind, near Rotterdam. His father was a practising physician in that city, his mother the daughter of a wine dealer of Middelharnis. The well-known landscape of Middelharnis, by Hobbema, in the National Gallery, shows the garden where van't Hoff often played in his boyhood.

Van't Hoff was sent to a private school, in which the education seems to have been of a liberal character, the usual scholastic subjects being relieved by sports, games, and physical exercises. Henry, as he was then called, to distinguish him from a brother likewise named Jacob, excelled in mathematics, and received commendation for his work in natural science. His mind, however, was not wholly occupied with his regular school studies, for at this time he was awarded prizes by a local musical society for singing and for pianoforte playing. Long country walks were a favourite recreation, and his letters show both his acute observation of nature and his keen appreciation of scenery. At the age of fifteen he entered the newly founded "Hoogere Burgerschool," a non-classical institution of the type of a German Real-schule.. Whilst constantly near the head of his class, he never succeeded in reaching the first place, if, indeed, he ever tried.

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* My information has been mostly derived from "J. H. van't Hoff's Amsterdamer Periode 1877—1895," by W. P. Jorissen and L. Th. Reicher (Helder, 1912), and in particular from the interesting biography by Professor Ernest Cohen, "Jacobus Henricus van't Hoff, sein Leben und Wirken" (Leipzig, 1912). Both of these works contain full bibliographies.

Here he received his first instruction in chemistry. A school companion relates that they were taught according to the old system of formulæ, the formula of water, for example, being HO, although they were told in the highest class that a new formulation with $H_2O$ was beginning to make headway. Practical instruction in chemistry was given in the school, and this evidently interested young van't Hoff, for he with some companions secretly repaired to the school on Sundays to finish their class exercises, and to perform additional unauthorised experiments. As they, boylike, enthusiastically chose to work with highly poisonous or explosive substances, their private investigations, when discovered, were brought to an abrupt end. Van't Hoff, however, continued his experiments at home, and conducted them on business-like lines, as he is reported to have charged spectators a small fee, which was expended in the purchase of fresh apparatus and material. A few months before van't Hoff completed his curriculum, the chemist Hoogewerff was appointed head of the school, and gave a sketch of the development of theories of organic chemistry, which, although too far advanced for the majority of the scholars, was welcomed and appreciated by van't Hoff. His leaving certificate reads as follows:

| | |
|---|---|
| Mathematics and mechanics ............ | Excellent |
| Physical science..... ........................ | Very good |
| History, etc. ................................... | Good |
| Languages and literature .................. | Satisfactory |
| Drawing ........... .............. ............ | Satisfactory. |

The following two years were spent by van't Hoff at the Polytechnic School of Delft. He had not yet decided what line of life he would take up, beyond that it should be practical. A holiday experience in a sugar factory, however, convinced him that technical chemistry was a somewhat monotonous occupation, and his inclination turned more and more towards pure science. He therefore on returning to the Polytechnic studied with increased zeal, and to such purpose that he received his diploma at the end of the second year, whereupon he left Delft for the University of Leiden.

What chiefly weighed with van't Hoff in moving to Leiden was the better opportunity afforded there for the study of the higher mathematics, the want of which he had greatly felt at Delft. At the University he frequented student society but little. On his rare appearances at the Debating Club, however, his comments on questions of the day and on topics of art or science provoked and enlivened discussion. Freedom and originality of thought were even then characteristic of him. Indeed, he complained in later years of his University studies that they were too matter-of-fact, took too little account of his being a man and not a mere organ for the acquisition of knowledge; and declared that under their influence he would have become a dried and shrivelled scientific conglomerate had it not been for the counter influence of the intensely subjective and personal Byron. The writers who influenced him at this impressionable period of his life were, on the philosophic-scientific side, Comte and Whewell, on the literary side, Burns and Heine. But Byron was his favourite and hero. References to Byron, quotations from Byron, abound in his letters, and together with much verse in his native tongue van't Hoff wrote many Byronic stanzas in English.

Van't Hoff now definitely decided on the study and prosecution of chemistry as his work in life, and since Leiden offered no special facilities in the subject, he passed his candidate's examination, a necessary step towards the doctorate, and left the University at the end of a year.

Kekulé's fame attracted him to Bonn. The romantic surroundings of the Rhine University town made a strong appeal to him. He wrote later: "In Leiden all was prose—the town, the country, the people. In Bonn all is poetry."

Only a year was spent by van't Hoff in Bonn. That he became unsettled, melancholy, even bitter, is clearly shown by the tone of his letters. He found Kekulé unsympathetic, but made a lasting friend in Walthère Spring, of Liège.

There can be little doubt that Kekulé's teachings on the constitution of organic substances deeply interested van't Hoff, and it was on Kekulé's advice that he continued his scientific studies elsewhere instead of accepting a technological or teaching post. van't Hoff's choice fell on the "Ecole de médecine," in Paris, where the genial Adolphe Wurtz directed the studies of his enthusiastic pupils, but before proceeding to France he entered the University of Utrecht for three months in order to pass the doctoral examination preliminary to the doctorate. The most noteworthy circumstance of van't Hoff's sojourn in Paris is that there he made the acquaintance of the Alsatian, Joseph Achille Le Bel, who a year later was to share with him the credit of the invention of the asymmetric carbon atom. van't Hoff apparently did little in the way of practical research while in Paris, and it is recorded of him, "Il était si tranquille qu'on ne faisait pas grande attention à lui."

In order to obtain his doctor's degree, van't Hoff re-matriculated in the University of Utrecht in October, 1874, and was promoted to his doctorate in December of the same year. His dissertation was entitled "A Contribution to our Knowledge of Cyanacetic Acid and Malonic Acid." It was of a routine character, and contained nothing beyond the powers of an ordinary advanced laboratory student. This is at first sight surprising, for van't Hoff had in the preceding September issued as a pamphlet his famous paper on space-formulæ. The original pamphlet was in Dutch, and bore the title, "An attempt to extend to space the present structural chemical formulæ, with an observation on the relation between optical activity and the chemical constitution of organic compounds." It argues well for the sound common sense of the young van't Hoff that he presented a humdrum piece of practical work for his dissertation rather than the startling innovation contained in his pamphlet, for the latter might have had an even worse fate than the equally famous thesis of Arrhenius, containing the first statement of the theory of electrolytic dissociation.

In giving this sketch of van't Hoff's educational career, I have made no attempt to treat it otherwise than in a superficial, mainly topographical, manner; and this because I fancy that the accidents of his education had little influence on his mental development. Now at the beginning of his productive career we find him a quiet, unassuming young man of twenty-two, with a physique by no means robust; reserved, but of agreeable manners; cultivated on many sides; with a taste for the writing of verse and for natural science, in particular entomology. He differed from the bulk of his academic contemporaries in being essentially a man of ideas, a thinker. He had pondered over the properties of the atoms, on their actions on one another at small distances, and over the problem of how the chemical and physical properties of compound molecules were to be conceived as a function of the nature of the constituent atoms and of their arrangement. The first tangible result of this cogitation was the laying of the foundation of stereochemistry.

It is a constant phenomenon, and always a fresh surprise in the history of science, to find a pioneer, capable, one might think, of any mental step, stopping short by a hand's breadth of some important discovery or generalisation. The driving force of the original idea exhausts itself, or the general state of knowledge fails in some particular, and years may have to elapse before a fresh mind with a new stimulus, and possibly a different goal, can take the required step. The early history of stereochemistry illustrates this peculiarity of scientific advance in striking fashion.

In a lecture published in 1860 Pasteur said: "We know, on the one hand, that the molecular structures of the two tartaric acids are asymmetric, and, on the other, that they are rigorously the same, with the sole difference of showing asymmetry in opposite senses. Are the atoms of the right acid grouped on the spirals of a dextrogyrate helix, or placed at the summits of an irregular tetrahedron? We cannot answer these questions." The ideas of the quadrivalent carbon atom and of molecular structure based upon it were still too novel and also too remote from Pasteur's practical line of thought, to enable him to take the short but, as it turned out, difficult step to the asymmetric carbon atom.

That the necessity for space-formulæ became increasingly felt is evident from the following quotations.

In 1867 Kekulé wrote: "The incompleteness of the old models may be avoided if, instead of arranging the four affinities of the carbon atom in a plane, we place them in the directions of hexagonal axes, so that they run out from the spherical atom and end in the planes of a tetrahedron."

A definite example of the use of space-formulæ is given by Paternò in 1869, who writes as follows:

"Three isomerides, $C_2H_4Br_2$, supposing that they really exist, can be easily explained, without the necessity of assuming with Butlerow a difference amongst the four affinities of the carbon atom, if we postulate that the four valencies of the atom of carbon are arranged in the sense of the four angles of a regular tetrahedron: then the first modification would have the two atoms of bromine (or any other univalent group) attached to the same atom of carbon; whilst in the other two modifications, the two atoms of bromine would be each attached to a different carbon atom, with the difference that in one case the two atoms of bromine would be symmetrically arranged, and in the other not."

Wislicenus in the same year clearly indicates the general nature and mode of solution of the problem in connexion with the lactic acids: "Facts like these will force us to explain the difference between isomeric molecules with the same structural formula by means of a different arrangement of their atoms in space, and to seek for definite ideas concerning this," a statement which he reiterates and emphasises in 1873.

These definite ideas were given practically at the same time by van't Hoff and by Le Bel, the former publishing his pamphlet in September, 1874, and the latter a paper in the *Bulletin de la Société Chimique* in November of the same year. One would naturally imagine that the idea which gave the key to the problem must have originated in one of the frequent discussions in Wurtz's laboratory, for here we have two young men parting at the end of June, and a few months later publishing separately a notion which was at the time generally regarded as something entirely novel and revolutionary. Yet van't Hoff tells us that no communication on the subject had passed between them. He says: "That shortly before this we had been working together in Wurtz's laboratory was purely fortuitous; we never exchanged a word about the tetrahedron there, though perhaps both of us cherished the idea in secret. To me it had occurred the year before, in Utrecht, after reading Wislicenus's paper on lactic acid."

In view of the passages I have quoted above from earlier workers, it might almost be asked: What, then, did van't Hoff and Le Bel discover? Wherein lies the merit of their work that they should be acclaimed as the originators of stereochemistry when the problem and the fundamental ideas seem to have been so clearly enunciated before them? On the one hand, the idea of the asymmetric structure of optically active molecules was given by Pasteur; on the other, Paternò uses tetrahedral carbon atoms to explain a case of isomerism in much the same way as they would be used to-day, except that he regards the carbon tetrahedra as not being capable of rotation round the axis joining their centres. Separate, these ideas remained unproductive; correlated, they became endowed with marvellous fertility. Van't Hoff and Le Bel's great contribution to stereochemistry was to define the conditions under which the asymmetric structure appeared, namely, when the carbon atom was attached to four different groups. Van't Hoff, in addition, boldly adopted the tetrahedron as the formal representation of the carbon atom in this new aspect; Le Bel, whose considerations are more general, only mentions it once in his paper. Not only did they state the bare principle, however; they showed it was a living one, drew deductions from it, applied it on all sides, and delivered it, in short, as an effective instrument into the hands of their fellow-workers in chemistry. Otherwise, like Avogadro's principle, it might have been forgotten, and for years perhaps have awaited some Cannizzaro to rediscover or revivify it.

It is of interest to quote van't Hoff's own words as to the origins of his conception and that of Le Bel, and as to the points in which they differed:

"On the whole, Le Bel's paper and mine are in accord; still, the conceptions are not quite the same. Historically, the difference lies in this, that Le Bel's starting point was the researches of Pasteur, mine those of Kekulé.

"The researches of Pasteur had made plain the connexion between optical activity and crystal-form, and had led to the idea that the isomerides of opposite rotatory power correspond with an asymmetric grouping and to its mirrored image. Indeed, the possibility of a tetrahedral grouping was suggested. Le Bel closely follows Pasteur, then, when he sees this grouping in the four atoms or radicles—inactive bodies all different—united to carbon.

"My conception is, as Baeyer pointed out at the Kekulé festival, a continuation of Kekulé's law of the quadrivalence of carbon, with the added hypothesis that the four valencies are directed towards the corners of a tetrahedron, at the centre of which is the carbon atom.

"Practically our ideas, so far as they concern the asymmetric carbon, amount to the same thing—explanation of the two isomerides by means of the tetrahedron and its image, disappearance of this isomerism when two groups become identical, through the resulting symmetry and identity of the two tetrahedra."

Le Bel's general treatment was more purely geometrical and in certain ways more thorough than that of van't Hoff, which was better calculated to appeal to chemists, and, indeed, gave the stamp to stereochemistry in its subsequent development. In detail the following points of difference between the authors may be noted. Le Bel accounts for the existence of internally compensated inactive forms, such as mesotartaric acid; van't Hoff, by means of the tetrahedra, clearly explains the nature of unsaturated inactive isomerides, such as maleic and fumaric acids.

The following lines contain a brief résumé of the original pamphlet of September, 1874. Van't Hoff shows that if we imagine the four affinities of the carbon atom to lie in a plane, the groups attached to them being fixed, and their positions not interchangeable, a great many more isomerides are predicted than actually exist. If, on the other hand, the affinities are not in a plane, but directed to the summits of a tetrahedron from its centre, the number of compounds predicted in general coincides with the number of compounds existing. His chief statements are given in the following terms:

(*a*) If the four affinities of a carbon atom are satisfied by four different univalent groups, two and not more than two tetrahedra are obtained, of which one is the mirror image of the other and cannot be superposed on it; that is, we encounter two isomeric structural formulæ in space.

(*b*) Each carbon compound which in the dissolved state effects a rotation of the plane of vibration of a polarised ray, contains an *asymmetric* carbon atom, that is, one whose affinities are satisfied by four different univalent groups. As examples, he gives lactic acid, aspartic acid, asparagine, and malic acid, with one asymmetric carbon atom; tartaric acid with two; the sugars, mannitol, etc., with at least one. Further, camphor and borneol, according to Kekulé's formulation, contain an symmetric carbon atom, and are correspondingly active.

The derivatives of optically active compounds lose their activity if the asymmetry of all the carbon atoms disappears; for example, inactive maleic acid from active malic acid, inactive succinic acid from active tartaric acid, inactive cymene from active camphor.

In a list of compounds the formulæ for which contain an asymmetric carbon atom, there are many cases in which the compound is not active. This may be accounted for in one of the following ways:

1. The compound may be an inactive mixture of two equally and oppositely active isomerides.

2. If the activity is small, it may be lost in the experimental error.

3. The condition "asymmetric carbon atom" may not in itself be sufficient, the nature of the different groups being of moment as well as their mere difference.

The principle that an optically active compound probably contains an asymmetric carbon atom gives the means of choosing between possible formulæ; for example, optically active primary amyl alcohol must have the formula $(CH_3)(C_2H_5)CH{\cdot}CH_2{\cdot}OH$. There is a certain degree of probability that an inactive compound contains no asymmetric carbon atom. Thus, the formula of citric acid is probably $CO_2H{\cdot}CH_2{\cdot}C(OH)(CO_2H){\cdot}CH_2{\cdot}CO_2H$, and not $CO_2H{\cdot}CH(OH){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$.

Formulæ are given for the simplest optically active monohydric alcohol, monobasic acid, dihydric alcohol, saturated hydrocarbon, and aromatic hydrocarbon; and attention is drawn to the fact that there are no optically active normal hydrocarbons, alcohols, or acids.

(*c*) If two doubly bound carbon atoms are each united to two radicles which differ from each other, two isomerides, hitherto unforeseen, are predicted; for example, maleic and fumaric acids.

In van't Hoff's pamphlet the carbon tetrahedra are figured exactly as they are met with now in text-books of organic chemistry.

A French translation of the paper appeared soon afterwards in the *Archives Néerlandaises*, and a condensed French account in the *Bulletin de la Société chimique*. Finally, a much expanded French pamphlet, "*La chimie dans l'espace*," was published at Rotterdam in May, 1875.

Disappointment followed the publication. Instead of his hypothesis provoking discussion, as he had hoped, it was received by the majority of chemists with indifference, if not with coldness. Wurtz, Spring, and Louis Henry wrote warm acknowledgments of its receipt, but made no attempt to discuss or criticise. Berthelot, whilst admitting the general interest of van't Hoff's formulæ, took up the ground that a complete representation of constitution involved a representation of the rotatory and vibratory movements of the atoms and groups, and was disposed to attribute optical activity to these movements. The physicist, Buys Ballot was the first to give serious attention to van't Hoff's theory, and in the *Maandblad voor Natuurwetenschappen* he published an open letter to van't Hoff, who replied in a paper (November, 1875), discussing many interesting points which had been raised in the letter. He gives, for example, the configurations of the ten isomeric saccharic acids. A cordial letter from Wislicenus then followed, suggesting that the pamphlet should be translated into German, which was done by Herrmann, and issued in 1877 under the title *Die Lagerung der Atome im Raume*, with a preface by Wislicenus. The German version, which differs in many ways from the original, was widely read, and van't Hoff's ideas now began to gain ground. Strenuous opposition by Kolbe, who at that time was tilting at graphic formulæ of every sort in a series of lively articles in the *Journal für praktische Chemie*, perhaps, if anything, increased their vogue by drawing more attention to the subject.

Meanwhile van't Hoff had graduated, and was on the look-out for a situation. He failed to obtain any teaching post as science master in a school, but in March, 1876, he succeeded in becoming assistant in the Veterinary College of Utrecht, there to teach chemistry and physics. He had command of good apparatus, and during the two years of his tenure of the office he worked at a variety of subjects, the substances obtained from storax claiming much of his attention. He wrote several stereochemical papers, one on carbon rings, one on Ladenburg's benzene formula, one on the direction of the valencies of the nitrogen atom, and one on the connexion between optical activity and constitution.

To this period belongs his book, "*Ansichten über die organische Chemie*," the preface of which is dated Utrecht, October, 1877. In itself the book is almost unreadable, but it affords the clearest evidence of the author's independence of thought, his keen eye for essentials, and the painstaking way in which he sought to isolate materials and problems of pure chemistry from the traditional associations which obscured them. The first part is purely systematic, and treats of the physical and chemical properties of organic substances regarded and classified as derivatives of methane. In the introduction to the second part (published in 1881), he expresses himself as follows:

"The purpose of the second part is to obtain a knowledge of the chemical nature of carbon in itself and of the changes which it undergoes when the element combines with other atoms or groups of atoms. To succeed in this purpose we must obtain a general view of the chemical reactions in which the carbon atom plays a part, and the changes in physical character which accompany them. If such a reaction is expressed by the general equation:

$$(\equiv\mathrm{C})\mathrm{X} + \mathrm{Y}\cdot\mathrm{Z} = (\equiv\mathrm{C})\mathrm{Y} + \mathrm{X}\cdot\mathrm{Z},$$

the knowledge of the reaction must include a knowledge of the heat change which accompanies the reaction, and of the velocity with which it takes place under given conditions, whilst a knowledge of the changes of property is attained by comparison of the physical nature of $(\equiv\mathrm{C})\mathrm{X}$ and $(\equiv\mathrm{C})\mathrm{Y}$. The reaction expressed above in general form may be followed out for particular carbon compounds $\left(\begin{smallmatrix}\alpha\\ \beta\\ \gamma\end{smallmatrix}\!\equiv\mathrm{C}\right)\mathrm{X}$ in the same two directions. What ultimately appears as independent of $\alpha$, $\beta$, $\gamma$ is the expression of the chemical nature of carbon in itself; the difference due to the changes of $\alpha$, $\beta$, $\gamma$ are, on the other hand, regarded as the changes which carbon undergoes when it combines with other atoms or groups of atoms."

In the text of the second part we find the beginnings of those studies in chemical thermodynamics and affinity which were afterwards pursued to such good purpose.

In September, 1877, van't Hoff was appointed lecturer in chemistry in the Town College of Amsterdam, which a month later was raised to the dignity of a State University. In June, 1878, at the age of twenty-six, he became ordinary Professor of Chemistry, Mineralogy, and Geology; and six months later he married Johanna Francina Mees, the daughter of a Rotterdam merchant, whom he had known from early youth.

Van't Hoff spent eighteen years in the University of Amsterdam. Although the old laboratory in which he worked was small and inconvenient, he refused a call in 1887 to the newly created Chair of Physical Chemistry in Leipzig, eventually filled by Ostwald. His teaching duties were onerous. With two assistants he had to give instruction in organic and inorganic chemistry, crystallography (which he had studied with Groth), mineralogy, geology, and palæontology, and to conduct practical classes for 100 medical and 20 science students. Notwithstanding this, the amount of practical work he executed and supervised was very great. The atmosphere of his laboratory may be described in the words of his assistant, van Deventer. "Whoever knows the Amsterdam laboratory knows that things do not take place there in any ordinary way. There is something mystical, something uncanny in the air. And this demonic something is the belief—one might call it the superstition if success had not so often followed it—the belief of van't Hoff that his fundamental idea, the analogy between chemical and physical phenomena, is profoundly true." Elsewhere van Deventer says: "It must be said that van't Hoff's work is in many ways more French than German. Soundness and solidity he certainly values, but he is in love with the idea in its general form, and his proofs are directed more towards establishing his idea in the world as a great rough block that cannot be overthrown, than to modelling and rounding it off—that he willingly leaves to others.

"This love of the idea is often found, too, in the experimental method which he adopted. Transition points were studied with an instrument which a well-trained physicist would only have used for preliminary experiments. Van't Hoff used it for the decisive investigation, and the proof is unimpeachable."

It is characteristic of van't Hoff's devotion to the idea that he chose as the subject of his inaugural address in Amsterdam, "The rôle of Imagination in Science," and strove to show how great a part imagination played in scientific investigation. He drew attention to the imposing number of scientific men with a leaning towards poetic and romantic invention, and closed his address with a quotation from Buckle: "There is a spiritual, a poetic, and, for aught we know, a spontaneous and uncaused element in the human mind, which ever and anon, suddenly and without warning, gives us a glimpse and a forecast of the future, and urges us to seize truth as it were by anticipation."

Following out the line of thought already indicated in his introduction to the "*Ansichten*," van't Hoff investigated various types of reaction velocity and chemical equilibrium, which he collected in his *Etudes de dynamique chimique*, published in 1884. It is true that much had been done by others in these fields of investigation; for example, in velocity by Harcourt and Esson and by Goldberg and Waage, and on the thermodynamical side by Horstmann and by Willard Gibbs, although the work of the latter was then unknown to van't Hoff, as indeed it was to chemists generally. Van't Hoff, however, systematised, exemplified, and applied the principles involved, and, in fact, left the subject of chemical dynamics much in the state in which we find it to-day. For example, he classified reactions into unimolecular, bimolecular, termolecular, according to the number of molecules taking part in the transformation. He showed how to determine the number of molecules taking part in a chemical action, and investigated secondary actions and disturbing influences. He discussed "temperature of inflammation." He introduced the symbol $\rightleftarrows$ for reversible actions. He introduced and illustrated the term "transition point," and showed the close analogy between the chemical "transition point" and the physical melting point, in particular as regards the effect of pressure. He stated clearly the *principe de l'équilibre mobile* as follows: "Every equilibrium between two systems is displaced by fall of temperature in the direction of that system in the production of which heat is developed." He showed that Berthelot's *principe du travail maximum* is only strictly true at the absolute zero. Finally, he devoted the last section of the book to a study of chemical affinity. He shows how affinity may be measured by electromotive force, how at a point of transition the work of affinity is zero, and constantly uses the important equation:

$$\frac{d \log_e K}{dT} = \frac{q}{2T^2},$$

although he does not prove it, merely stating that it had been deduced in a rigorous manner from the principles of thermodynamics. I remember having read these *Études* in 1885 or 1886, and I can well recall the mingled feeling of revelation and bewilderment which the book produced on me. I had perused such books on theoretical and physical chemistry as were then available, but had derived comparatively little satisfaction from them. Here, I thought, was the real thing at last, hard to comprehend, certainly, but something definite. What I understood was excellent. What I did not quite succeed in understanding seemed, somehow, even better.

Arrhenius, at that time personally unknown to van't Hoff, in reviewing the *Études*, wrote as follows: "This work, which is of the greatest interest, consists of two essentially different parts: the first experimental, the second theoretical. The former is, however, of quite subordinate significance, notwithstanding the many peculiar and interesting phenomena discussed in it. In the latter portion the author displays an extraordinary talent for bringing a great series of different facts under one point of view, and he succeeds with relatively scanty experimental material in developing an imposing and harmonious scheme for the whole subject of chemical influence and action. Although the author has already gained a great name by his power of wresting secrets from Nature, his former efforts are placed entirely in the shade by this work. An enormous perspective has been opened up for future investigation. There are, however, but few workers in the promising field, though possibly this will shortly be remedied; for since Helmholtz, who sets the fashion in physical circles, has turned his attention of late years to such subjects, it will probably not be long before eager investigators are working at them."

A few years later this prediction was fulfilled, chiefly through the instrumentality of Ostwald, the first occupant of the chair of physical chemistry in Leipzig.

In the *Études* we have the first appearance of osmotic pressure from the physico-chemical point of view. Through his distinguished countryman, the botanist, Hugo de Vries, van't Hoff had become acquainted with Pfeffer's osmotic measurements. He at once saw the thermodynamic importance of the conception, and used it in conjunction with the lowering of vapour pressure to calculate the affinity of certain salts for their water of crystallisation. In the following year (1885) he published in the *Archives néerlandaises* a paper bearing the title "*L'équilibre chimique dans les systèmes gazeux ou dissous à l'état dilué, gazeux ou dissous*"; and in 1886 he published in the Transactions of the Swedish Academy three memoirs, entitled "*Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous,*" "*Une propriété générale de l'équilibre chimique,*" and "*Conditions électriques de l'équilibre chimique.*"

In these papers van't Hoff had arrived at the complete analogy between gases and substances in dilute solution. He tells us that in giving the proof of his equation:

$$\frac{d \log_e K}{dT} = \frac{q}{2T^2},$$

by means of reversible cycles for dilute gaseous systems, it occurred to him that with the help of semi-permeable membranes all the reversible processes which make the application of thermodynamics to gases so simple might as readily be applied to substances in dilute solution. It at once followed that the osmotic pressure must vary with the temperature according to Gay-Lussac's law. Pfeffer's measurements for 1 per cent. sugar solutions seemed to confirm this conclusion, although they were scarcely sufficiently accurate to afford absolute proof of the relation. Then Pfeffer had shown that the osmotic pressure was proportional to the concentration, that is, Boyle's law was followed as well as Gay-Lussac's, and it was possible to write for dilute solutions an equation similar to that for gases, namely:

$$PV = RT.$$

The only thing left was to calculate $R$, the solution-constant, and compare it with the gas-constant. van't Hoff did this for sugar solutions from Pfeffer's measurements, and found to his surprise that the value was identical with that of the gas-constant. At first he looked upon this identity as a mere coincidence, but further consideration showed it to be fundamental, and that osmotic and gaseous pressure were always equal, when molecular concentration and temperature were equal, that, in short, Avogadro's law held without alteration for substances in dilute solution as well as for gases, and that the molecular weights of dissolved substances could be determined on the same theoretical grounds as those of gases.

Raoult had in the meantime shown empirically how molecular weights might be determined from the lowering of the freezing point, and van't Hoff was now in a position to give the theoretical justification of this method, by deducing thermodynamically from Avogadro's law and the properties of the solvents, the quantitative rules for the lowering of vapour tension, the depression of the freezing point, and the elevation of the boiling point of solutions.

It should be noted that van't Hoff was from the first very careful to point out that all these relations were strictly applicable only to very dilute solutions, to "ideal solutions," as he calls them, and that he never claimed the theory of osmotic pressure as a complete theory of solutions. He definitely stated, indeed, in his address to the German Chemical Society (*Ber.*, 1894, **27**, 15): "It is not even necessary to choose osmotic pressure as the starting point [of these relations]; the whole might be deduced as readily from Henry's law or from Raoult's law. Only osmotic pressure is a very simple and handy expression for the whole behaviour, and its physical meaning is very readily stated and grasped, thus: If a substance in a state of dilution exists in surroundings into which it can expand by diffusion, then, at a given temperature, the pressure which will prevent this diffusion is dependent only on the number of dissolved molecules, and not on the nature of the medium." To van't Hoff's mind the real theory of the intimate nature of solutions begins where the simple laws *cease* to be obeyed. In a sense this is true, and a good example of what it means is afforded by the early history of the osmotic pressure theory. Van't Hoff had found that the value of the osmotic constant was not for all substances equal to the gas constant $R$. With his customary skill in handling such matters, he wrote the equation for these substances as follows:

$$PV = iRT,$$

using a factor $i$, which was thus the measure of the abnormality of the substance. The work of Arrhenius supplied two years later the explanation of the abnormality in the case of the great class of electrolytic solutions. The abnormally great value of $i$ for such solutions was held by Arrhenius to be due to the molecular concentration in such solutions being greater than had theretofore been accepted. According to his theory of electrolytic dissociation, some of the original dissolved molecules had split up under the influence of the solvent into simpler positive and negative ions, so that the total number of molecules was increased, the excess of $i$ over 1 being the measure of the increase. This, then, is a contribution to the theory of solution for a certain class of solutions, and it appears to me that every future contribution will be of the same nature, dependent on the nature of the solvent and dissolved substance, and therefore of a different scope entirely from van't Hoff's generalisation.

Two distinct points may be noted in connexion with the papers just referred to. First, there is the introduction of the conception of osmotic pressure into thermodynamics generally, and the use of semipermeable membranes for reversibly changing the concentration of solutions. Second, there is the special application of the conception in deducing the simple general laws for ideal solutions. As van't Hoff himself has said, it would be possible to substitute for osmotic pressure in the purely thermodynamical treatment some other magnitude which is proportional to it, but it may be confidently predicted that the conception once introduced, and through which such advances have been made, will never be discarded.

One often encounters among chemists the impression that van't Hoff was essentially a mathematician, or at least a man of mathematical formulæ, who cared nothing for atoms or molecules. Nothing could be further from the truth. Van't Hoff's actual knowledge of mathematics is surpassed, I fancy, by the average honours B.Sc. student of to-day. His ability in this direction lay rather in the power of handling the mathematical tool for his own purposes. But, as is apparent from the passages I have already quoted, the essential thing for him is the reciprocal action and influence of atoms and molecules. The nature of osmotic pressure, as well as its law, was of profound interest to him. He first of all conceived it as having its origin in the mutual attractions of solvent and solute molecules, but soon discarded this view for one of molecular bombardment in analogy with the kinetic theory of gases. This kinetic theory of the origin of osmotic pressure, despite criticisms, still seems superior to any other that has been proposed, and awaits further development.

Although, as has been said, the papers comparing dilute substances with gases were published in 1885, it was only in 1887 that the ideas became generally known. Ostwald, the organiser of the campaign in favour of the new ideas of van't Hoff and Arrhenius, associated himself with the former in founding the *Zeitschrift für physikalische Chemie*, in the first volume of which the fundamental papers of the two pioneers of modern physical chemistry appear.

With the foundation of this journal van't Hoff's scientific life may be said to have reached its climax. His fame became worldwide, and many honours awaited him. A new chemical laboratory, built according to his designs, was opened in 1891, and many foreign students visited him who could not have been accommodated in the old building. With the increase of his department, van't Hoff found that he had to devote more and more time to administrative duties, as is the universal experience of the heads of large laboratories. He naturally disliked to see his leisure for personal research slip away from him, and asks, "Besides men whose duty it is to teach, and who, if they have time and inclination for it, may prosecute research, is there not room for another class of men whose duty should be to investigate, and who, if they pleased, might also teach?" In the spring of 1895 a position of the latter kind was offered to him in Berlin. Great efforts were made by his colleagues in the University of Amsterdam to induce the Government of the Netherlands to retain him in Holland on similar terms, but these efforts were unsuccessful. Van't Hoff, in the spring of 1896, moved to Berlin, as a member of the Prussian Academy of Sciences and as a Professor in the University. His academic duties were of the lightest, one lecture a week being all that was required of him. His research work was carried out in a small laboratory situated in a pleasant suburb of Berlin. Here his chief collaborator was his friend and former pupil, Meyerhoffer. Often in conjunction with younger men, they studied the physical chemistry of the Stassfurt salt deposits, and similar phase-rule problems.

Such work, though of much general and special interest, is not to be placed on a par with van't Hoff's former achievements. It is true that in plan and in performance it may be taken as a model for an investigation on the grand scale, yet one cannot but entertain the feeling that a lesser man than van't Hoff, for example, his own countryman, Bakhuis Roozeboom, might have carried it to an equally successful conclusion. The conception of solid solutions (1890) is van't Hoff's last contribution to novel chemical ideas.

Van't Hoff had now more leisure, not only for practical research, but for travel. He has left an interesting journal of his impressions of America in 1901. In December of the same year he journeyed to Stockholm to receive the first Nobel Prize for Chemistry; and it may be recalled that he delivered the Raoult Memorial Lecture here in 1902.

The death of Meyerhoffer in 1906 affected him deeply, and later in the same year his own health began to give way. He himself writes: "My health, almost invariably good, seemed in the summer of 1906 to be even better than usual. In early spring I had visited the neighbourhood of Vesuvius at the time of the eruption, and returned home rejuvenated. Hay-fever, for many years my bugbear, had vanished, and it appeared as if my Bonn student days, with all their poetry, had, comet-like, returned. And yet I found in all this something abnormal, and recalled to mind a saying of a former medical colleague, that a feeling of specially good health in one's later years is a bad omen. In October came the first indications of what six months later developed into an illness which for a time laid me aside from all work." From that date van't Hoff had to spare himself, a thing peculiarly distasteful to a man of his active mind and temperament. He brought his work on the salt-deposits to a close, and devoted himself to the lighter labour of revising some of his older books, and projecting new ones.

His last scheme of investigation was a study of the intimate nature of the chemical processes occurring in plants. To this end he began in 1909 a research on reversible enzymatic action, and published a preliminary account in the *Sitzungsberichte* of the Prussian Academy (October, 1909, and November, 1910). These admirable fragments show a last flash of van't Hoff's illuminating genius. The clearness of the theoretical conceptions, the simplicity of the experimental execution recall the best period of his activity. He proved that the action of the enzyme emulsin in the formation and decomposition of glucosides was that of an ordinary catalyst in accordance with the mass-action law, the rates of the reverse reactions alone being affected and the point of equilibrium remaining unchanged.

The last experiments were carried out in a small private laboratory which had been built for him on the Imperial Crown-lands at Dahlem. Here from time to time he was able to do a little work, but the progress of his malady slowly enfeebled him. The entry in his diary for December 11th, 1910, reads, "Article on 'Teaching and Research' finished: a last effort." On the evening of March 1st, 1911, he died peacefully.

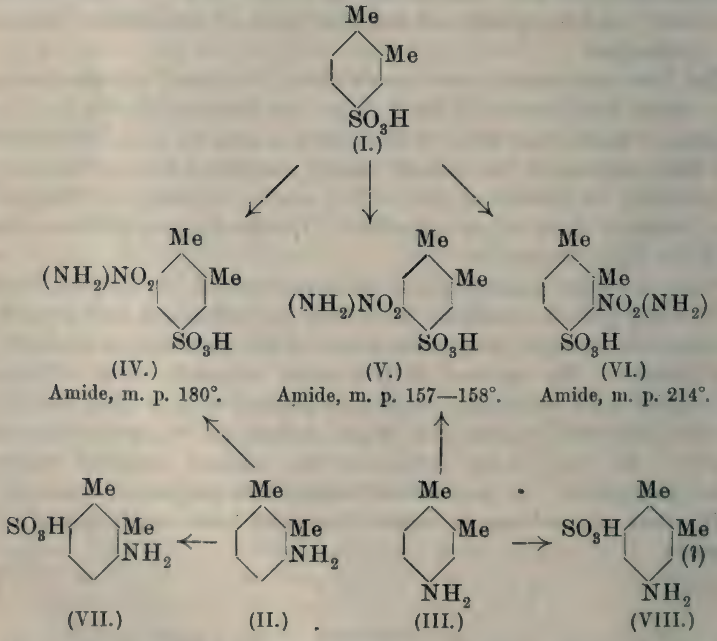
With no great mathematical or experimental attainment, with no striking gift as a teacher, van't Hoff yet influenced and moulded the current thought, and even much of the practice, of chemistry for decades. He set out with a clear scientific ideal. Native inspiration and unflagging ardour in pursuit of this ideal led him to the discovery of principles of the widest and most far-reaching import. He was, in my judgment, the greatest chemical thinker of his generation. If any should dispute this judgment, I can only reply that our science is indeed favoured when such dispute is possible.

# CXX.—*Derivatives of* o-*Xylene.*

### By John Lionel Simonsen.

In spite of the careful investigation of Crossley and Renouf (T., 1909, **95**, 202), the preparation of 3-nitro-*o*-xylene is still a somewhat laborious process. As the author required a considerable quantity of this substance for certain experiments, it occurred to him that it might possibly be obtained more readily by the nitration of *o*-xylene-4-sulphonic acid and subsequent elimination of the sulphonic acid group. Although this expectation was not realised, the experiments seem of sufficient importance to warrant publication.

When *o*-xylene-4-sulphonic acid is treated with nitric acid under the conditions described in the experimental part of this paper (p. 1151), the three isomeric nitro-*o*-xylene-4-sulphonic acids are formed. The orientation of these acids is a matter of considerable difficulty, owing to the fact that no method could be devised to eliminate the sulphonic acid group:



On reduction, the nitro-sulphonic acids are converted into the corresponding amino-acids, and it was found possible to orientate these acids in the following manner. When *o*-3-xylidine (II) is sulphonated, it yields a mixture of two sulphonic acids, which may be separated by means of their barium salts. Since one of these acids was completely different from the amino-acids (IV, V, or VI) obtained by the reduction of the nitro-acids derived from *o*-xylene-4-sulphonic acid, it follows that it must be o-3-*xylidine*-6-*sulphonic acid* (VII).

The second acid isolated in this sulphonation was found to be identical with the amino-acid obtained by the reduction of the nitro-sulphonic acid, yielding an amide melting at 180°; this acid must therefore possess the constitution indicated by the formulæ IV or VI. In order to decide which of these two formulæ was correct, the amino-acid was diazotised and converted into the xylenolsulphonic acid, which on fusion with potassium hydroxide yielded a dihydroxyxylene giving a purple colour with ferric chloride and a fluorescein when treated with phthalic anhydride. Unfortunately this phenol was not obtained in sufficient quantity to purify, but it probably consisted of 3:5-dihydroxy-*o*-xylene (*Annalen*, 1904, **329**, 305). From this is follows that the amino-sulphonic acid must be o-3-*xylidine*-5-*sulphonic acid*, and the nitro-acid which yields an amide melting at 180° must be 3-nitro-*o*-xylene-5-sulphonic acid (IV).

In order to determine the constitution of the two remaining nitro-acids the sulphonation of *o*-4-xylidine was investigated, when it was found that two sulphonic acids were formed. One of these was identical with the amino-acid obtained by the reduction of the nitro-acid, yielding an amide melting at 157—158°. Only one formula is possible for this acid, which must be o-4-*xylidine*-5-*sulphonic acid* (V). This was confirmed by eliminating the amino-group from a specimen of the amino-sulphonic acid prepared from *o*-4-xylidine, when *o*-xylene-4-sulphonic acid was obtained and identified by means of its amide.

As to the constitution of the second acid formed in the sulphonation of *o*-4-xylidine, it has unfortunately proved impossible to arrive at any definite conclusion. The acid was diazotised and the xylenolsulphonic acid fused with potassium hydroxide, when a dihydroxyxylene was isolated, giving an intense purple coloration with ferric chloride; it was not sufficient for any further investigation. It is probable that this acid is *o*-4-xylidine-6-sulphonic acid (VIII). An acid possessing this constitution has already been described by Cazeneuve and Moreau (*Bull. Soc. chim.*, 1898, [iii], **19**, 21). It was prepared by the sulphonation of *s*-dixylylcarbimide [$NH : Me_2 = 1 : 3 : 4$]. This experiment has been repeated, and it has been found that the products are identical with those obtained by the sulphonation of *o*-4-xylidine. Since, however, *o*-4-xylidine-

6-sulphonic acid is formed in much the larger amount, it is probable that it was this acid which was described by Cazeneuve and Moreau.

It now only remains to consider the constitution of the third acid obtained by the nitration of *o*-xylene-4-sulphonic acid. There is only one possible formula for this acid, and it must be 3-*nitro-o-xylene-4-sulphonic acid* (VI).

Since the amino-sulphonic acids described in this paper do not possess melting points, and since all attempts to prepare derivatives which might have proved useful for identification purposes proved unsuccessful, it was necessary to identify the acids or their salts by careful examination under a polarising microscope, and I wish to express my thanks to my colleague, Dr. M. Stuart, Professor of Geology, for assisting me in this part of the work.

## EXPERIMENTAL.

### 3-*Nitro-o-xylene-5-sulphonic Acid.*

This acid was obtained in the form of its sparingly soluble *barium* salt by the nitration of *o*-xylene-4-sulphonic acid (see p. 1152). The barium salt was purified by repeated crystallisation from hot water, in which it is only sparingly soluble; it separates on cooling in glistening, prismatic needles, which apparently contain three molecules of water of crystallisation:

0·7974 lost 0·0437 at 110°. $H_2O = 5·5$.
0·9678 * gave 0·3409 $BaSO_4$. $Ba = 20·7$.
0·4921 † „ 0·1866 $BaSO_4$. $Ba = 22·3$.
$C_{16}H_{16}O_{10}N_2S_2Ba,3H_2O$ requires $Ba = 21·1$.
$C_{16}H_{16}O_{10}N_2S_2Ba,H_2O$ „ $Ba = 22·3$.
Loss of $2H_2O$ requires $H_2O = 5·5$ per cent.

3-*Nitro-o-xylene-5-sulphonic acid* was isolated from the pure barium salt in the usual manner, when it was obtained in slender needles, which were somewhat hygroscopic, the crystals liquefying on exposure to the air. For this reason no attempt was made to analyse the acid. The *chloride* prepared from the barium salt by treatment with phosphorus pentachloride crystallises from a mixture of benzene and light petroleum in large, glistening, irregular plates, which melt at 69—70°:

0·1247 gave 0·0729 AgCl. $Cl = 14·4$.
$C_8H_8O_4NSCl$ requires $Cl = 14·2$ per cent.

The *amide* crystallises from dilute alcohol in fine, hair-like needles, melting at 180°:

0·1059 gave 13·1 c.c. $N_2$ at 34° and 760 mm. $N = 13·0$.
$C_8H_{10}O_4N_2S$ requires $N = 12·2$ per cent.

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* Air-dried. † Dried at 110°.

### o-3-*Xylidine-5-sulphonic Acid.*

(1) *From 3-Nitro-o-xylene-5-sulphonic Acid.*—When the nitrosulphonic acid is reduced with tin and hydrochloric acid, only a very small yield of the amino-acid is obtained, owing to the simultaneous formation of chloro-derivatives. Reduction by means of an alkaline solution of ferrous sulphate was found, however, to give good results. In one such experiment, the barium salt (3·6 grams) was dissolved in hot water, and treated with an aqueous solution of the calculated amount of ferrous sulphate, barium hydroxide being added until the solution was just alkaline. After heating on the water-bath for two hours, the excess of baryta was removed by carbon dioxide, and the filtered solution concentrated, when the *barium* salt (2·8 grams) separated in slender needles. For analysis it was purified by crystallisation from a little water:

0·0855 lost 0·004 at 120°. $H_2O = 4·7$.
0·2038* gave 0·0821 $BaSO_4$. Ba = 23·7.
0·0818† „ 0·0338 $BaSO_4$. Ba = 24·3.
$C_{16}H_{20}O_6N_2S_2Ba,3H_2O$ requires Ba = 23·4.
$C_{16}H_{20}O_6N_2S_2Ba,1\frac{1}{2}H_2O$ „ Ba = 24·3.
Loss of $1\frac{1}{2}H_2O$ requires $H_2O = 4·6$ per cent.

*Barium* o-3-*xylidine-5-sulphonate* is excessively soluble in cold water, and shows very little tendency to crystallise. It is also characterised by the fact that it reddens very rapidly on exposure to the air.

o-3-*Xylidine-5-sulphonic acid* crystallises from hot water, in which it is fairly readily soluble, in slender needles radiating from a centre containing apparently one molecule of water of crystallisation, which is not lost at 100°. Like its barium salt, it is characterised by the extreme rapidity with which it reddens on exposure to the air, the change being much more rapid than in the case of its isomerides. It does not melt or decompose at 315°:

0·1363 gave 8·0 c.c. $N_2$ at 32° and 762 mm. N = 6·3.
$C_8H_{11}O_3NS,H_2O$ requires N = 6·4 per cent.

(2) *From* o-3-*Xylidine.*—From the sulphonation products of *o*-3-xylidine (see p. 1152), a barium salt was isolated which possessed all the properties of the barium salt described above, and a careful microscopic examination showed that they were identical. No difference either could be detected in the amino-sulphonic acid isolated from this barium salt. Both the barium salt and the free acid showed the property of rapid reddening on exposure to the air which is so characteristic of this substance.

*Diazotisation of* o-3-*Xylidine-5-sulphonic Acid.*—In order to prepare *o*-3-xylenol-5-sulphonic acid, the amino-acid (1·7 grams) was dissolved in water, and after the addition of barium nitrite (0·74 gram), sulphuric acid (0·74 gram) was gradually added to the well-cooled mixture. After remaining in the cold for one hour, the mixture was heated on the water-bath until all evolution of nitrogen had ceased (about thirty minutes). The excess of sulphuric acid was removed by the calculated quantity of barium carbonate, the solution filtered and evaporated, when o-3-*xylenol*-5-*sulphonic acid* was obtained as a viscid oil, which showed no signs of crystallising. When fused with potassium hydroxide at 320—330°, very little charring took place, and a dihydroxyxylene was isolated in the usual manner, which gave with ferric chloride a purple coloration, and after heating with phthalic anhydride, its alkaline solution was strongly fluorescent. Owing to the very small yield, this compound could not be obtained in a pure state, but there can be no doubt that it was 3:5-dihydroxy-*o*-xylene (*Annalen*, 1904, **329**, 305).

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* Air-dried. † Dried at 120°.

### 3-*Nitro*-o-*xylene*-4-*sulphonic Acid.*

This acid was isolated from the nitration of *o*-xylene-4-sulphonic acid in the form of its *amide* (see p. 1151). This was purified by crystallisation from alcohol, in which it is only sparingly soluble, and separates in large, prismatic needles, which melt at 214°. For analysis it was dried at 100°:

0·1058 gave 12·5 c.c. $N_2$ at 33° and 763 mm. N = 12·6.

$C_8H_{10}O_4N_2S$ requires N = 12·2 per cent.

In order to obtain the free acid, the amide (5 grams) was mixed with concentrated hydrochloric acid (15 c.c.), and heated in a sealed tube for four hours at 150—160°. The product was poured into water, filtered from a trace of carbonaceous matter, and evaporated to dryness on the water-bath, when a mixture of the nitro-sulphonic acid and ammonium chloride was obtained. To isolate the pure acid, the mixture was dissolved in water, and boiled with excess of baryta until no further odour of ammonia was perceptible, the barium exactly precipitated with sulphuric acid, and the filtered solution evaporated to dryness, when 3-*nitro*-o-*xylene*-4-*sulphonic acid* was obtained in needles, which, after crystallisation from a little water, were dried at 120° and analysed:

0·1317 gave 5·8 c.c. $N_2$ at 30° and 763 mm. N = 4·8.

$C_8H_9O_5NS,3H_2O$ requires N = 4·9 per cent.

The *barium* salt crystallises in glistening, fatty-looking needles. For analysis it was dried at 130°:

0·2882 gave 0·1081 $BaSO_4$. Ba = 22·1.

$C_{16}H_{16}O_{10}N_2S_2Ba,H_2O$ requires Ba = 22·3 per cent.

3-o-*Xylidine-4-sulphonic Acid.*—This acid was prepared by the reduction of the corresponding nitro-acid by means of ferrous sulphate. It was purified by crystallisation from hot water, in which it is only very sparingly soluble, when it separated in octahedral prisms, which blacken but do not melt at 300°:

0·1122 gave 6·2 c.c. $N_2$ at 29° and 765 mm. N = 6·2.

$C_8H_{11}O_3NS,H_2O$ requires N = 6·4 per cent.

The *barium* salt crystallises from water, in which it is sparingly soluble, in rectangular prisms possessing a high refractive index. It only slowly becomes pink on exposure to the air:

0·4471 lost 0·0249 at 120°. $H_2O = 5·6$.

0·2437 * gave 0·104 $BaSO_4$. Ba = 25·1.

$C_{16}H_{20}O_6N_2S_2Ba,2\frac{1}{2}H_2O$ requires $H_2O = 6·1$.

$C_{16}H_{20}O_6N_2S_2Ba,\frac{1}{2}H_2O$ „ Ba = 25·1 per cent.

### 4-*Nitro*-o-*xylene-5-sulphonic Acid.*

This acid was isolated in small quantities in the form of its amide from the nitration of *o*-xylene-4-sulphonic acid (see p. 1151). The *amide* crystallises from alcohol, in which it is somewhat readily soluble, in small, hard, prismatic needles, melting at 157—158°:

0·1117 gave 12·7 c.c. $N_2$ at 33° and 763 mm. N = 12·1.

$C_8H_{10}O_4N_2S$ requires N = 12·2 per cent.

4-*Nitro*-o-*xylene*-5-*sulphonic acid* was obtained from the amide by hydrolysis with hydrochloric acid, as was described above in the case of the 4-sulphonic acid, when it was isolated in bayonet-shaped, somewhat hygroscopic needles. As the amount at the disposal of the author was small, it was not further examined.

### o-4-*Xylidine-5-sulphonic Acid.*

(1) *From 4-Nitro-o-xylene-5-sulphonic Acid.*—When this acid is reduced by means of alkaline ferrous sulphate, the amino-acid is readily isolated in the form of its barium salt.

The *barium* salt separates from hot water, in which it is readily soluble, in highly characteristic rectangular plates or spangles, which show straight extinction. It crystallises with eight molecules of water of crystallisation, which it loses at 125°:

0·2757 † gave 0·0944 $BaSO_4$. Ba = 20·1.

0·5638 lost 0·1154 at 125°. $H_2O = 20·4$.

$C_{16}H_{20}O_6N_2S_2Ba,8H_2O$ requires Ba = 20·2; $H_2O = 20·2$ per cent.

o-4-*Xylidine*-5-*sulphonic acid* crystallises in tablets which are only very sparingly soluble in hot water. It blackens at 280°, but does not decompose at 300°. For analysis it was dried at 120°:

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* Dried at 120°.

† Air-dried.

0·205 gave 0·243 $BaSO_4$. S = 16·3.

$C_8H_{11}O_3NS$ requires S = 15·9 per cent.

(2) *By the Sulphonation of* o-4-*Xylidine and* s-*Dixylylcarbimide* [NH : $Me_2$ = 1 : 3 : 4].—When *o*-4-xylidine was sulphonated, as described on p. 1153, the highly characteristic barium salt of *o*-4-xylidine-5-sulphonic acid was readily separated from the reaction mixture. Careful examination both of the barium salt and the acid showed that it was identical with the acid obtained by the nitration of *o*-xylene-4-sulphonic acid.

This acid was also obtained when the above-mentioned carbamide was sulphonated (see p. 1153).

*Diazotisation of* o-4-*Xylidine*-5-*sulphonic Acid.*—In order to eliminate the amino-group and obtain *o*-xylene-4-sulphonic acid, the amino-sulphonic acid (prepared from *o*-4-xylidine) (0·2 gram) was dissolved in sulphuric acid (0·2 gram), and after the addition of a little alcohol (about 3 c.c.) amyl nitrite (5 c.c.) was added to the well-cooled solution. After an hour the mixture was heated on the water-bath, when the white solid which was suspended in the liquid passed into solution, and nitrogen was evolved. The product was poured into water, the sulphuric acid removed by means of barium carbonate, and the filtered solution evaporated on the water-bath, when the barium salt of *o*-xylene-4-sulphonic acid separated. This was converted into the amide in the usual manner; after crystallisation from alcohol the latter melted at 143—144°, and showed no depression when mixed with the amide of this acid obtained from another source.

### o-3-*Xylidine*-6-*sulphonic Acid.*

This acid was obtained by the sulphonation of *o*-3-xylidine (see p. 1152) and was separated in the form of its *barium* salt; the latter is readily soluble in water, and crystallises in glistening, octahedral pyramids, which rapidly effloresce in the air. This salt also shows very markedly the property of supercooling:

0·3101 lost 0·0363. $H_2O$ = 11·7.

0·2738 gave 0·115 $BaSO_4$. Ba = 24·7.

$C_{16}H_{20}O_6N_2S_2Ba,H_2O$ requires Ba = 24·7.

Loss of $4H_2O$ requires $H_2O$ = 11·5 per cent.

o-3-*Xylidine*-6-*sulphonic acid* separates from water in bunches of sheaf-like needles, which do not change colour in the air. It does not darken when heated to 305°:

0·1195 gave 7·3 c.c. $N_2$ at 28° and 763 mm. N = 6·7.

$C_8H_{11}O_3NS$ requires N = 7·0 per cent.

### o-4-*Xylidine*-6-*sulphonic Acid* (?).

This acid was separated in the form of its sparingly soluble barium salt from the sulphonation of *o*-4-xylidine and of *s*-dixylylcarbamide (see p. 1153). The *barium* salt separates from hot water in large, well-developed plates, belonging probably to the orthorhombic system, the corner angle measuring approximately 90°. The crystals, on exposure to the air, slowly become pink. For analysis the salt was dried at 120°, when no loss of weight occurred:

0·228 gave 0·0946 $BaSO_4$. Ba = 24·3.

$C_{16}H_{20}O_6N_2S_2Ba,1\frac{1}{2}H_2O$ requires Ba = 24·3 per cent.

o-4-*Xylidine*-6-*sulphonic acid*, obtained from the barium salt, crystallises from hot water in aggregates of plates, which do not easily redden in the air. When heated in a capillary tube it darkens at 283°, and melts and decomposes at 294°. It apparently contains two molecules of water of crystallisation, which it does not lose at 120°:

0·1634 gave 0·1653 $BaSO_4$. S = 13·9.

$C_8H_{11}O_3NS,2H_2O$ requires S = 13·7 per cent.

When the acid is diazotised with barium nitrite, and the diazo-compound boiled with water, the xylenolsulphonic acid was obtained in prismatic needles, which gave a bright blue coloration with ferric chloride. An attempt was made to fuse it with potassium hydroxide in order to isolate the dihydroxyxylene, but no satisfactory result was obtained. The trace of dihydroxyxylene that was isolated gave a purple coloration with ferric chloride, but it was too small in quantity for further examination.

### *Nitration of* o-*Xylene*-4-*sulphonic Acid.*

In carrying out the nitration of *o*-xylene-4-sulphonic acid, the following method was found to give the most satisfactory results. Fuming nitric acid (D 1·5) (255 grams) was well cooled in a freezing mixture, and the sulphonic acid (85 grams) was gradually added with constant shaking. The sulphonic acid slowly passed into solution, and after remaining in ice for six hours, the mixture was allowed to remain at the room temperature (30°) for two days, and then poured into a large volume of water. A flocculent precipitate (2·5 grams) separated; this was collected and reserved for further examination (see below).

In order to isolate the nitro-sulphonic acids, the acid liquor was evaporated as far as possible under diminished pressure on the water-bath, the last traces of nitric acid being removed over potassium hydroxide in a vacuum desiccator. The semi-solid mass thus obtained was dissolved in water and treated with barium hydroxide, the excess of barium hydroxide removed by carbon dioxide, and the pale yellow solution of the barium salts was concentrated on the water-bath, when the sparingly soluble barium salt of 3-nitro-*o*-xylene-5-sulphonic acid separated in prismatic needles (yield 34 grams). On concentrating the mother liquor, a second crop of the same substance was obtained.

Since the filtrate on further concentration yielded no definitely crystalline product, the mixture of barium salts (85 grams) was carefully dried, and, after mixing with excess of phosphorus pentachloride, heated on the water-bath for an hour. On decomposing the mixture with ice-water, the acid chloride (64 grams) separated as an oil, which was isolated by means of ether, dried, and without further purification converted into the amide with ammonium carbonate. The crude, brown amide obtained in this way was subjected to a careful process of fractional crystallisation from alcohol, when it was separated into two main fractions: (*a*) a very sparingly soluble amide melting at 214° (15 grams), the amide of 3-nitro-*o*-xylene-4-sulphonic acid, and (*b*) a more readily soluble amide melting at 157—158° (2·8 grams), the amide of 4-nitro-*o*-xylene-5-sulphonic acid. The mother liquors contained a mixture of amides (18 grams), which could not be purified.

It was mentioned above that when the nitration products were poured into water a small quantity of an insoluble substance separated. This was crystallised from benzene, from which it separated in yellow leaflets resembling picric acid. When heated fairly rapidly, it sinters at 170°, and melts and decomposes at 183—185°:

0·1307 gave 17·8 c.c. $N_2$ at 28° and 759 mm. N = 14·8.

$C_8H_8O_4N_2$ requires N = 14·3 per cent.

This new *dinitro-*o*-xylene*, which must contain one of the nitro-groups in the side-chain, is readily soluble in alcohol, but is precipitated from it as an oil, from which the original substance could not be isolated. It is soluble in sodium carbonate, and is not reprecipitated on acidification. Further experiments are in progress with the view of elucidating the constitution of this substance.

### *Sulphonation of* o*-3-Xylidine.*

*o*-3-Xylidine (12 grams) was mixed with sulphuric acid (36 c.c.), and heated for two hours at 160°, and finally at 180° for one hour. The brown product was cooled and poured into water, when a large amount of solid (10 grams) separated, and was collected. The filtrate was carefully examined, but no pure substance could be isolated.

For the purposes of purification, the above-mentioned solid was converted into its barium salt, and subjected to a long process of crystallisation. It was found to consist of a mixture of the barium salts of *o*-3-xylidine-6-sulphonic acid (3 grams) and *o*-3-xylidine-5-sulphonic acid (6 grams). Indications of the presence of a third salt were obtained, but it could not be isolated in sufficient quantity for purification.

### *Sulphonation of* o-4-*Xylidine.*

*o*-4-Xylidine was sulphonated under similar experimental conditions to those just described. On pouring the product into water, a voluminous, white precipitate separated (8 grams). This was collected, and the filtrate was found to contain a small quantity of *o*-4-xylidine-5-sulphonic acid.

In order to separate the sparingly soluble mixture of sulphonic acids, recourse was again had to the difference in solubility of the barium salts. On allowing a dilute solution to remain, it slowly deposits the barium salt of *o*-4-xylidine-6-sulphonic acid in large, rectangular plates, some of them more than 4 mm. in size (yield 3 grams). The mother liquor from which this barium salt separated was concentrated, when the barium salt of *o*-4-xylidine-5-sulphonic acid was obtained in beautiful spangles (7 grams).

### *Sulphonation of s-Dixylylcarbamide* ($NH : Me_2 = 1 : 3 : 4$).

The carbamide (2·5 grams) was mixed with sulphuric acid (10 c.c.), and heated at 160° until all evolution of carbon dioxide had ceased (compare *Bull. Soc. chim.*, 1896, [iii], **19**, 21). The product was examined as has been described above, and was found to consist of a mixture of *o*-4-xylidine-5-sulphonic acid and *o*-4-xylidine-6-sulphonic acid, the former acid predominating.

The author wishes to thank the Research Fund Committee for a grant which defrayed part of the expense of this investigation.

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# CXXI.—*The Relative Activities of Certain Organic Iodo-compounds with Sodium Phenoxide in Alcoholic Solution. Part I. Some Normal Primary Alkyl Iodides.*

By DAVID SEGALLER.

DURING the past few decades a considerable amount of research has been undertaken with the object of determining the relative reactivities of various organic substances, and there can be little doubt that the results obtained will have a powerful influence on the development of future theories of chemical reactivity. In general, reaction between organic compounds is much more complex than that which takes place between inorganic substances, so that it is necessary to deal only with the simplest forms of reaction when studying the reactivities of organic compounds. Among such reactions are those which take place between organic iodides and sodium derivatives of alcohols and phenols, and a certain amount of work has already been done in this direction by Hecht, Conrad, and Bruckner (*Zeitsch. physikal. Chem.*, 1899, **4**, 273), Menschutkin (*ibid.*, 1890, **5**, 589), Brusoff (*ibid.*, 1900, **34**, 129). A valuable summary of these results is given by Burke and Donnan (T., 1904, **85**, 555), who investigated the reactivities of some alkyl iodides with silver nitrate. The results obtained by the latter authors do not agree with those found by some of the other investigators, for example, Hecht, Conrad, and Bruckner (*ibid.*), and Menschutkin (*ibid.*). It might here be pointed out that in Burke and Donnan's reaction mixture silver iodide was precipitated, and the change of phase so produced may possibly have influenced the velocity of the reaction. Conrad and Bruckner, in continuation of their investigation on the velocity of ether formation (*Zeitsch. physikal. Chem.*, 1891, **7**, 274), made a few measurements of velocity-constants, in which the reaction mixture consisted of alkyl iodide (they measured only methyl, ethyl, and propyl iodides), sodium ethoxide, and phenol. Measurements of the reactivities of some organic halogen compounds have also been made by Slator (T., 1904, **85**, 1286), who used sodium thiosulphate. Preston and Jones (T., 1912, **101**, 1930) measured the rates of reaction of methyl, ethyl, propyl, and allyl iodides with certain tertiary bases, and found some anomaly in the behaviour of methyl iodide.

The author of the present communication considered it desirable to undertake a more extended study of the reactivities of the organic iodides than any yet recorded, and for the purposes of this investigation sodium phenoxide was selected as the reagent with which the relative reactivities were to be measured. The sodium phenoxide was prepared by a modification of Forcrand's method (*Ann. Chim. Phys.*, 1893, [vi], **30**, 60). Considerable difficulty was encountered in obtaining the substance in a sufficient state of purity, the only satisfactory process being to prepare it as directed by Forcrand, then to crystallise it from methyl alcohol or acetone, and to heat the product in a current of pure dry hydrogen for some hours at about 150°. The substance prepared in this manner is quite colourless. (Found, Na=19·78, 19·73. Calc., Na=19·82 per cent.)

The following table and curve (Fig. 1) show the relative reactivities of those primary normal alkyl iodides measured by Menschutkin, Hecht, and Conrad, and Burke and Donnan:

| | Menschutkin. | Hecht and Conrad. | Burke and Donnan. |
|---|---|---|---|
| Methyl | 11·40 | 61·72 | 1·35 |
| Ethyl | 10·1 | 4·87 | 3·25 |
| Propyl | 1·43 | 1·71 | 1·52 |
| Butyl | 1·38 | — | 1·00 |
| Amyl | — | — | — |
| Hexyl | — | — | — |
| Heptyl | 1·38 | 1·04 | — |
| Octyl | 1·08 | 1·00 | — |

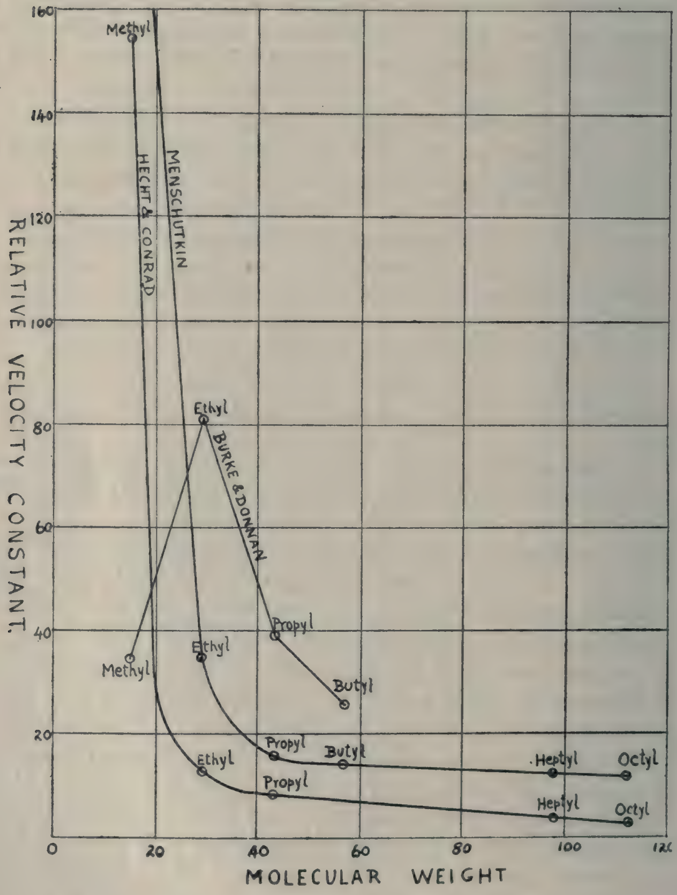
The present communication deals only with the normal primary alkyl iodides, the results obtained with the secondary and tertiary alkyl iodides being reserved for a future paper.

The alcohol used was the commercial "absolute," which was twice distilled from fresh quicklime. It was then boiled under reflux with metallic calcium turnings for some hours, and finally distilled from the calcium into bottles provided with drying tubes.

The iodides used were in most cases Kahlbaum's preparations, whilst the normal hexyl and heptyl iodides were prepared by the author by standard methods. The purification of these iodides was generally carried out as follows: The substance was washed with dilute sodium hydroxide, then with water, and finally dried over calcium chloride in the usual way, and fractionated. In many cases (especially with the higher homologues) it is not possible to obtain a colourless liquid in this way, even when fractionation is done in a vacuum. To free the substance completely from dissolved iodine the liquid was shaken with freshly ignited silver powder. In this way a quite colourless product of correct boiling point was obtained in every instance, and was immediately used for the reaction. It was found that after the iodide had been thoroughly purified in this manner, the best way to preserve it was to keep a little silver powder in the bottle containing the liquid. Some *iso*propyl iodide (which, as is well known, becomes coloured with great rapidity even out of contact with air and in the dark), so purified and preserved by the author, was found after two years to be quite colourless and of correct boiling point.

To prevent evaporation in the thermostat, the water was covered with a layer of lubricating oil. It might not be out of place to mention a slight improvement in the thermo-regulator, which was of a modified Ostwald type and kept the temperature of the bath constant to 1/50°. The side-tube containing the micrometer screw was inclined downwards instead of being in the usual horizontal position, and in this way the tendency for tiny air bubbles to be

Fig. 1.



sucked in was avoided, beside having the advantage that if the bath has to be cooled and re-heated, the side-tube becomes completely filled with mercury before the latter rises further in the capillary. This is not always the case with regulators where the micrometer screw is at right angles to the stem.

The thermometers and all measuring vessels used were "Standard."

The measurements of the velocity-coefficients were carried out as follows: Solutions of known strength (generally $N$) of the iodide under consideration and the sodium phenoxide, both in absolute ethyl alcohol, were prepared. Of each of these solutions 50 c.c. were transferred into a stoppered Jena-glass bottle, which was then thoroughly shaken, and 10 c.c. of this mixture transferred into each of eight Jena-glass test-tubes, which were immediately tightly stoppered with rubber corks. The test-tubes fitted into a brass stand, which was lowered so as to rest on a tray in the bath, the tubes being almost completely immersed. After the mixture had attained the temperature of the bath (generally in fifteen minutes), the time was noted, and a test-tube rapidly taken out and emptied into a beaker containing some ice and an amount of $N/20$-hydrochloric acid almost sufficient to neutralise any unchanged sodium phenoxide (this was ascertained by a parallel experiment). Phenolphthalein was then added, and the neutralisation completed from a burette. This was taken as the "zero" of the measurements. After various intervals of time, varying according to the reactivity of the substance used, other test-tubes were dealt with in this way. The velocity-constant was calculated according to the usual formula for a bimolecular reaction.

$t$ = time in minutes.
$a$ = concentration of sodium phenoxide.
$b$ = " " alkyl iodide in gram-molecules.
$x$ = amount of sodium phenoxide changed in time $t$.
$K$ = velocity-constant.

In the following experiments the initial concentrations were equal, so that $a=b$ and $K=\frac{1}{t}\cdot\frac{x}{a(a-x)}$.

so that if $a$ = number of c.c. of acid required to neutralise the mixture at the zero,
$a-x$ = number of c.c. of acid required to neutralise the mixture after time $t$.

Then since $a$ and $(a-x)$ are proportional to the concentrations of the sodium phenoxide at times 0 and $t$ respectively, if

$y$ = number of c.c. of the acid being used at the time which would be required to neutralise the amount of sodium phenoxide contained by each mixture before commencement of experiment,

$$\text{then } K=\frac{1}{t}\cdot\frac{x}{(a-x)}\ \frac{y}{a},$$

$$\text{let } \quad k=\frac{1}{t}\cdot\frac{x}{a-x},$$

$$\text{then } K=k\cdot\frac{y}{a}.$$

All the following experiments were carried out at 42·5°.

### *Methyl Iodide.*

Each mixture contained 5 c.c. of $N$-methyl iodide and 5 c.c. of $N$-sodium phenoxide. The acid used was $N/5$-hydrochloric acid, therefore $y=25$.

I.

Zero = 22·40 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 10 | 17·16 | 5·24 | 0·03054 |
| 15 | 15·44 | 6·96 | 0·03001 |
| 20 | 13·95 | 8·45 | 0·03029 |
| 25 | 12·90 | 9·50 | 0·02945 |
| 30 | 11·76 | 10·64 | 0·03016 |
| 35 | 10·88 | 11·52 | 0·03025 |

$k$ mean = 0·03012

$\therefore K=k\times 25/22{\cdot}4 = 0{\cdot}03362$

II.

Zero = 20·80 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 10 | 16·23 | 4·57 | 0·02816 |
| 15 | 14·65 | 6·15 | 0·02800 |
| 20 | 13·35 | 7·45 | 0·02790 |
| 25 | 12·30 | 8·50 | 0·02764 |
| 30 | 11·38 | 9·42 | 0·02754 |
| 40 | 9·85 | 10·95 | 0·02780 |

$k$ mean = 0·02784

$K=k\times 25/20{\cdot}8 = 0{\cdot}03358$

Another experiment in which $N/2$-solutions were used gave $K=0{\cdot}03514$. Further investigation, however, showed that comparable results can only be obtained if the initial concentrations are the same for all substances under comparison.

In this investigation $N$-solutions were therefore used throughout.

In the following tables full data are given only for one experiment, and the mean coefficient for another experiment. In the case of *n*-heptyl iodide material from two different sources was used, and in this case data for both experiments are given.

### *Ethyl Iodide.*

This was purified as above. Each mixture contained 5 c.c. of $N$-ethyl iodide and 5 c.c. of $N$-sodium phenoxide. Acid $=N/5$; $y=25$.

I.

Zero = 21·80 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 60 | 15·90 | 5·90 | 0·006184 |
| 90 | 14·00 | 7·80 | 0·006190 |
| 120 | 12·60 | 9·20 | 0·006085 |
| 150 | 11·30 | 10·50 | 0·006194 |
| 180 | 10·40 | 11·40 | 0·006080 |

$k$ mean = 0·006124

$K = k \times 25/21·8$ = 0·007023

II.

$K$ mean = 0·007003

### n-*Propyl Iodide.*

This was purified as above. Each mixture consisted of 5 c.c. of $N$-propyl iodide and 5 c.c. of $N$-sodium phenoxide. The acid used was 1·108$N$/5-hydrochloric acid, therefore $y = 27·7$.

I.

Zero = 22·45 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 45 | 20·40 | 2·05 | 0·002233 |
| 90 | 18·65 | 3·80 | 0·002263 |
| 120 | 17 60 | 4·85 | 0·002296 |
| 215 | 15·20 | 7·25 | 0·002219 |
| 240 | 14·52 | 7·93 | 0·002274 |

$k$ mean = 0·002257

$K = k \times 27·7/22·45$ = 0·002788

II.

$K$ mean = 0·002800

### n-*Butyl Iodide.*

This was purified as above. Each mixture consisted of 5 c.c. of $N$-butyl iodide and 5 c.c. of $N$-sodium phenoxide. Acid = $N/5$; $y = 25$.

I.

Zero = 23·90 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 90 | 19·50 | 4·40 | 0·002504 |
| 210 | 15·72 | 8·18 | 0·002478 |
| 270 | 14·48 | 9·42 | 0·002409 |
| 330 | 13·30 | 10·60 | 0·002416 |
| 510 | 10·70 | 13·20 | 0·002419 |

$k$ mean = 0·002441

$K = k \times 25/23·9$ = 0·002544

II

$K$ mean = 0·002566

### n-*Amyl Iodide.*

The substance was purified by shaking with freshly ignited silver powder just before use. It was then quite colourless, and boiled at 156° (corr.).

On account of its costly nature, the mixtures in this case consisted of only 2 c.c., composed of a mixture of equal volumes of *N*-amyl iodide and *N*-sodium phenoxide. The acid was *N*/10-hydrochloric acid, therefore $y=10$.

I.

Zero = 9·40 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 100 | 8·46 | 0·94 | 0·001111 |
| 200 | 7·74 | 1·66 | 0·001072 |
| 300 | 7·13 | 2·27 | 0·001061 |
| 400 | 6·56 | 2·84 | 0·001082 |
| 500 | 6·13 | 3·27 | 0·001067 |
| 600 | 5·72 | 3·68 | 0·001073 |

$k$ mean = 0·001078

$K = k \times 10/9{\cdot}4 = 0{\cdot}001147$

II.

$K$ mean = 0·001126

*n*-Amyl iodide gives much lower results than would have been expected.

### n-*Hexyl Iodide.*

The substance was colourless and boiled at 180°.

Each mixture consisted of 5 c.c. of *N*-hexyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5; $y=25$.

I.

Zero = 24·25 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 80 | 20·35 | 3·90 | 0·002395 |
| 180 | 17·02 | 7·23 | 0·002359 |
| 240 | 15·38 | 8·87 | 0·002400 |
| 300 | 14·20 | 10·05 | 0·002359 |
| 400 | 12·55 | 11·70 | 0·002330 |
| 500 | 11·20 | 13·05 | 0·002333 |

$k$ mean = 0·002362

$K = k \times 25/24{\cdot}25 = 0{\cdot}002436$

II.

$K$ mean = 0·002438

### n-*Heptyl Iodide.*

The substance was purified as above. It was quite colourless, and boiled at 204°.

Each mixture contained 5 c.c. of $N$-heptyl iodide and 5 c.c. of $N$-sodium phenoxide. The acid was $N/10$; $y=50$.

#### I.

Zero = 47·60 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 105 | 38·32 | 9·28 | 0·002306 |
| 225 | 31·50 | 16·10 | 0·002272 |
| 285 | 28·85 | 18·25 | 0·002285 |
| 345 | 26·50 | 21·10 | 0·002309 |
| 495 | 22·30 | 25·30 | 0·002289 |

$k$ mean = 0·002292

$K=k\times 50/47{\cdot}6$ = 0·002408

#### II.

A different preparation gave the following results.

Acid = $N/5$; $y=25$.

Zero = 23·85 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 100 | 19·33 | 4·52 | 0·002338 |
| 200 | 16·24 | 7·61 | 0·002342 |
| 300 | 14·03 | 9·82 | 0·002333 |
| 400 | 12·42 | 11·43 | 0·002300 |
| 500 | 11·14 | 12·71 | 0·002281 |
| 600 | 9·95 | 13·90 | 0·002327 |

$k$ mean = 0·002320

$K = k\times 25/23{\cdot}85$ = 0·002432

### n-*Octyl Iodide.*

The substance was purified as described above.

Each tube contained 5 c.c. of $N$-octyl iodide and 5 c.c. of $N$ sodium phenoxide. The acid was $N/10$; $y=50$.

#### I.

Zero = 47·50 c.c.

| $t$. | $a-x$. | $x$. | $k$. |
|---|---|---|---|
| 110 | 38·00 | 9·50 | 0·002220 |
| 210 | 32·25 | 15·25 | 0·002251 |
| 280 | 29·25 | 18·25 | 0·002229 |
| 340 | 26·75 | 20·75 | 0·002281 |
| 500 | 22·10 | 25·40 | 0·002298 |
| 600 | 22·00 | 27·50 | 0·002291 |

$k$ mean = 0·002270

$K=k\times 50/47{\cdot}5$ = 0·002389

#### II.

$K$ mean = 0·002382

### *Cetyl Iodide.*

The substance was purified by repeated crystallisation from alcohol, and dried in a vacuum. It then consisted of white, pearly scales, melting at 22°, and boiling at 212°/745 mm.

Each mixture contained 5 c.c. of *N*-cetyl iodide and 5 c.c. of sodium phenoxide. The acid was $N/5$; $y=25$.

I.

Zero = 24·20 c.c.

| *t.* | *a – x.* | *x.* | *k.* |
|---|---|---|---|
| 80 | 20·73 | 3·47 | 0·002092 |
| 120 | 19·37 | 4·83 | 0·002077 |
| 330 | 14·95 | 9·25 | 0·002062 |
| 400 | 13·24 | 10·96 | 0·002069 |
| 500 | 11·93 | 12·27 | 0·002056 |
| 600 | 10·80 | 13·40 | 0·002070 |

$k$ mean = 0·002071

$K = k \times 25/24 \cdot 2$ = 0·002140

II.

$K$ mean = 0·002185

The following numbers and curve (Fig. 2) express the relative reactivities of the substances dealt with in this paper, as measured by sodium phenoxide in alcoholic solution:

| | | | |
|---|---|---|---|
| Methyl | 14·66 | *n*-Hexyl | 1·08 |
| Ethyl | 3·03 | *n*-Heptyl | 1·05 |
| *n*-Propyl | 1·21 | *n*-Octyl | 1·01 |
| *n*-Butyl | 1·15 | *n*-Cetyl | 1·00 |
| *n*-Amyl | 0·49 | | |

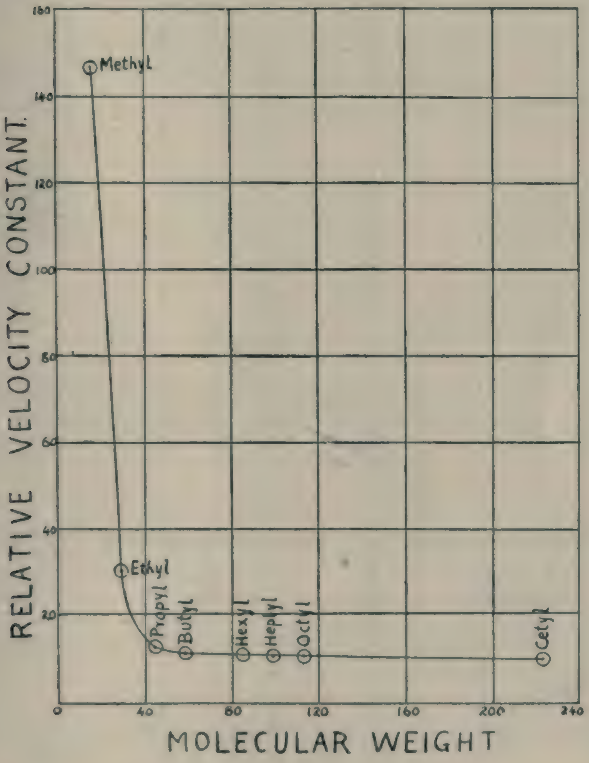
When $M/K$ is plotted against $M$, the graph below (Fig. 3) is obtained. The deviation, however, from the rectilinear relation is greater than at first sight, owing to the relatively large variation of $M/K$ with $M$. The greatest deviations appear in the cases of ethyl and amyl iodides, the latter lying quite off the line in the diagram.

### *The Effect of Initial Concentration on the Velocity-coefficient.*

As mentioned above, it was found that comparable results could be obtained only when the initial concentration of each reaction mixture was the same in each case, and for that reason the experiments described have dealt only with solutions the initial concentrations of which were kept normal.

This effect of initial concentration on the magnitude of the velocity-coefficient is a point of great importance, and does not seem to have been investigated in a large number of reactions in which velocity of reactions has been studied. Hecht and Conrad, in their work on the rate of ether formation (*loc. cit.*), found that a decrease in concentration of the sodium ethoxide raised the velocity-coefficient, but that a decrease in the concentration of the alkyl iodide had very little effect in that direction. These authors also found that their results could be connected fairly well by the formula $K_v = K_1 + a\log v$, where $a$ is a constant, and $v$ the reciprocal of the initial equivalent concentration.

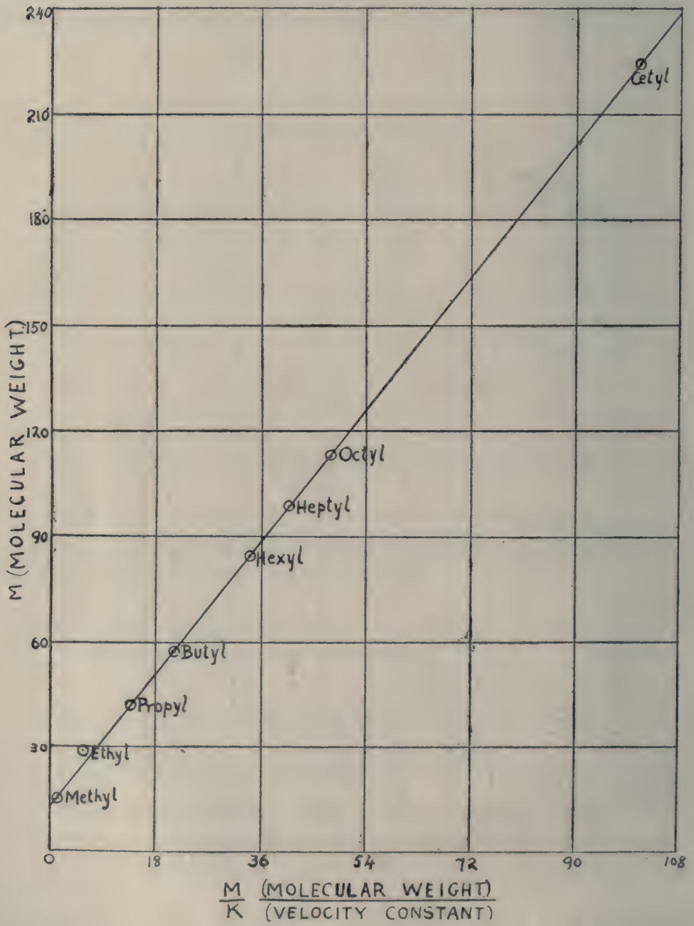
FIG. 2.



Burke and Donnan (*loc. cit.*) found that a decrease in the concentration of the alkyl iodide raised the velocity-coefficient, but that this was diminished by a decrease in the concentration of the silver nitrate. Slator (*loc. cit.*), on the other hand, does not find any appreciable alteration in the velocity-coefficient by change in the initial concentration.

With the object of obtaining more information on this subject, some measurements were made of the velocity-coefficient, using solutions of *n*-propyl iodide and of sodium phenoxide less and greater than normal. The experiments fall into three groups:

FIG. 3.



(*A*) The initial concentrations of both the phenoxide and the iodide altered, but using equivalent initial concentrations.

(*B*) The initial concentration of the iodide kept at normal, but that of the phenoxide altered.

(*C*) The initial concentration of the phenoxide kept at normal, but that of the iodide altered.

In the cases of *B* and *C*, the velocity-coefficient was calculated by means of the equation:

$$K = \frac{1}{(a-b)t} \cdot \log_e \frac{(a-x)}{(b-x)} \cdot \frac{b}{a},$$

where *a*, *b*, *c* have the same significance as above.

### *A*.

Each mixture contained 10 c.c. of *N*/2-propyl iodide and 5 c.c. of *N*/2-sodium phenoxide. The acid was *N*/10.

Zero = 23·64 c.c.

| *t*. | *a* − *x*. | *x*. | *K*. |
|---|---|---|---|
| 100 | 19·99 | 3·61 | 0·003616 |
| 200 | 17·29 | 6·31 | 0·003648 |
| 300 | 15·47 | 8·13 | 0·003504 |
| 400 | 14·05 | 9·55 | 0·003400 |
| 500 | 12·72 | 10·88 | 0·003420 |
| 600 | 11·60 | 12·00 | 0·003448 |
| | | *K* mean = | 0·003506 |

Each mixture contained 10 c.c. of *N*/5-propyl iodide and 10 c.c. of *N*/5-sodium phenoxide. The acid was *N*/10.

Zero = 18·60 c.c.

| *t*. | *a* − *x*. | *x*. | *K*. |
|---|---|---|---|
| 100 | 17·16 | 1·44 | 0·004193 |
| 250 | 15·48 | 3·12 | 0·004031 |
| 405 | 14·00 | 4·60 | 0·004074 |
| 465 | 13·36 | 5·24 | 0·004217 |
| 650 | 13·00 | 5·60 | 0·004026 |
| 701 | 11·82 | 6·78 | 0·004092 |
| | | *K* mean = | 0·004415 |

Each mixture contained 10 c.c. of *N*/10-propyl iodide and 10 c.c. of *N*/10-sodium phenoxide. The acid was *N*/20.

Zero = 18·20 c.c.

| *t*. | *a* − *x*. | *x*. | *K*. |
|---|---|---|---|
| 300 | 15·94 | 2·26 | 0·005197 |
| 400 | 15·26 | 2·94 | 0·005291 |
| 600 | 14·20 | 4·00 | 0·005164 |
| 800 | 13·22 | 4·98 | 0·005174 |
| 1000 | 12·38 | 5·82 | 0·005166 |
| 1200 | 11·62 | 6·58 | 0·005182 |
| | | *K* mean = | 0·005196 |

As shown in the following table, the above results are fairly well represented by Hecht and Conrad's equation: $K_v = K_1 + a \log v$:

| Concentration of sodium phenoxide. | Concentration of *n*-propyl iodide. | *K* (found.) | $K_v = K_1 + a \log v$. $a = 0·002299$. |
|---|---|---|---|
| *N* | *N* | 0·002800 | 0·002899 |
| *N*/2 | *N*/2 | 0·003506 | 0·003498 |
| *N*/5 | *N*/5 | 0·004415 | 0·004413 |
| *N*/10 | *N*/10 | 0·005196 | 0·005105 |

## *B.*

Each mixture contained 5 c.c. of *N*-propyl iodide and 5 c.c. of *N*/2-sodium phenoxide. Acid = *N*/10.

| *t.* | *a – x.* | *b – x.* | *K.* |
|---|---|---|---|
| 0 | 23·10 | 48·10 | — |
| 30 | 19·12 | 44·12 | 0·003427 |
| 90 | 17·35 | 42·35 | 0·003526 |
| 125 | 16·02 | 41·02 | 0·003309 |
| 180 | 13·74 | 38·74 | 0·003392 |
| 240 | 11·84 | 36·84 | 0·003426 |
| 300 | 10·18 | 35·18 | 0·003376 |
|  |  |  | *K* mean = 0·003409 |

Each mixture contained 10 c.c. of *N*-propyl iodide and 10 c.c. of *N*/5-sodium phenoxide. Acid = *N*/10.

| *t.* | *a – x.* | *b – x.* | *K.* |
|---|---|---|---|
| 0 | 17·83 | 97·83 | — |
| 30 | 15·70 | 95·70 | 0·004421 |
| 50 | 14·50 | 94·50 | 0·004295 |
| 70 | 13·40 | 93·40 | 0·004267 |
| 100 | 11·97 | 91·97 | 0·004203 |
| 120 | 11·15 | 91·15 | 0·004150 |
| 150 | 9·68 | 89·68 | 0·004361 |
|  |  |  | *K* mean = 0·004283 |

Each mixture contained 20 c.c. of *N*-propyl iodide and 20 c.c. of *N*/10-sodium phenoxide. Acid = *N*/10.

| *t.* | *a – x.* | *b – x.* | *K.* |
|---|---|---|---|
| 0 | 18·20 | 198·20 | — |
| 20 | 16·50 | 196·50 | 0·005098 |
| 30 | 15·61 | 195·61 | 0·005205 |
| 50 | 14·28 | 194·28 | 0·004942 |
| 67 | 13·15 | 193·15 | 0·004957 |
| 81 | 12·20 | 192·20 | 0·005071 |
| 125 | 10·12 | 190·12 | 0·004840 |
|  |  |  | *K* mean = 0·005019 |

| Concentration of sodium phenoxide. | Concentration of *n*-propyl iodide. | *K* (found.) | $K_v = K_1 + a \log v$. $a = 0·002122$. |
|---|---|---|---|
| *N* | *N* | 0·002800 | 0·002800 |
| *N*/2 | *N* | 0·003409 | 0·003445 |
| *N*/5 | *N* | 0·004283 | 0·004289 |
| *N*/10 | *N* | 0·005019 | 0·004928 |

## *C.*

Each mixture contained 5 c.c. of 4*N*-propyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5.

| *t.* | *a – x.* | *b – x.* | *K.* |
|---|---|---|---|
| 0 | 20·70 | 95·70 | — |
| 30 | 15·92 | 90·92 | 0·002400 |
| 60 | 12·17 | 87·17 | 0·002430 |
| 75 | 10·84 | 85·84 | 0·002390 |
| 85 | 9·90 | 84·90 | 0·002421 |
| 95 | 9·00 | 84·00 | 0·002462 |
| 100 | 7·97 | 82·97 | 0·002452 |

*K* mean = 0·002426

Each mixture contained 5 c.c. of 2*N*-propyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5.

| *t.* | *a – x.* | *b – x.* | *K.* |
|---|---|---|---|
| 0 | 22·18 | 47·18 | — |
| 60 | 16·45 | 41·45 | 0·002802 |
| 90 | 14·26 | 39·26 | 0·002862 |
| 120 | 12·62 | 37·62 | 0·002808 |
| 174 | 10·82 | 35·82 | 0·002568 |
| 220 | 8·82 | 33·82 | 0·002678 |
| 250 | 8·12 | 33·12 | 0·002600 |

*K* mean = 0·002708

Each mixture contained 5 c.c. of *N*/2-propyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5.

| *t.* | *a – x.* | *b – x.* | *K.* |
|---|---|---|---|
| 0 | 23·46 | 10·96 | — |
| 44 | 22·20 | 9·70 | 0·003042 |
| 150 | 20·06 | 7·56 | 0·002806 |
| 260 | 18·20 | 5·70 | 0·003073 |
| 420 | 16·55 | 4·05 | 0·003071 |
| 485 | 16·13 | 3·63 | 0·003010 |
| 564 | 15·70 | 3·20 | 0·002940 |

*K* mean = 0·002900

Each mixture contained 5 c.c. of *N*/5-propyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5.

| *t.* | *a – x.* | *b – x.* | *K.* |
|---|---|---|---|
| 0 | 24·40 | 4·40 | — |
| 56 | 23·60 | 3·60 | 0·003732 |
| 110 | 23·02 | 3·02 | 0·003610 |
| 150 | 22·58 | 2·58 | 0·003799 |
| 230 | 22·05 | 2·05 | 0·003596 |
| 259 | 21·84 | 1·84 | 0·003669 |
| 455 | 20·78 | 0·78 | 0·003617 |

*K* mean = 0·003670

| Concentration of sodium phenoxide. | Concentration of *n*-propyl iodide. | *K* (found.) | $K_v = K_1 + a \log v$. $a = 0{\cdot}0009$. |
|---|---|---|---|
| *N* | 4*N* | 0·002426 | 0·002338 |
| *N* | 2*N* | 0·002708 | 0·002609 |
| *N* | *N* | 0·002800 | 0·002880 |
| *N* | *N*/2 | 0·002990 | 0·003151 |
| *N* | *N*/5 | 0·003670 | 0·003509 |

Although the equation used in the tables above answers well, the results can be represented even more satisfactorily by an equation of the type: $K = p + q/c$, where $p$ and $q$ are constants independent of the concentration $c$. In the relation between the velocity-coefficient and the initial concentration, where the phenoxide is kept at constant initial concentration and that of the iodide varied, then $p = 0{\cdot}00258$ and $q = 0{\cdot}000218$.

| Concentration of *n*-propyl iodide. | *K* (found.) | $K = p + q/c$. |
|---|---|---|
| 4*N* | 0·002426 | 0·002634 |
| 2*N* | 0·002708 | 0·002689 |
| *N* | 0·002806 | 0·002798 |
| *N*/2 | 0·002990 | 0·003016 |
| *N*/5 | 0·003670 | 0·003670 |

*Mean Velocity-coefficients for* n-*Propyl Iodide and Sodium Phenoxide.*

| Concentration of sodium phenoxide. | Concentration of *n*-propyl iodide. | Mean value of *K*. | $K_v = K_1 + a \log v$. |
|---|---|---|---|
| *N* | *N* | 0·002800 | 0·002806 |
| *N* | 4*N* | 0·002426 | 0·002338 |
| *N* | 2*N* | 0·002708 | 0·002609 |
| *N* | *N*/2 | 0·002990 | 0·003151 |
| *N* | *N*/5 | 0·003670 | 0·003509 |
| *N*/2 | *N*/2 | 0·003506 | 0·003498 |
| *N*/2 | *N* | 0·003409 | 0·003445 |
| *N*/5 | *N*/5 | 0·004415 | 0·004413 |
| *N*/5 | *N* | 0·004283 | 0·004289 |
| *N*/10 | *N*/10 | 0·005196 | 0·005105 |
| *N*/10 | *N* | 0·005019 | 0·004928 |

The above table brings out the following facts:

(1) An increase in the initial concentration of either the phenoxide or the iodide produces a decrease in the value of *K*, whereas a decrease in the initial concentration of either the phenoxide or the iodide produces an increase in the value of *K*. This differs from the results of Hecht and Conrad, who found that only a decrease in the concentration of the ethoxide produces any considerable increase in the value of *K*.

Burke and Donnan, on the other hand, find a decrease in *K* with decrease in concentration of the silver nitrate.

(2) The initial concentration of the phenoxide exerts a much greater influence on the reaction-velocity than that of the iodide. In the case of change of concentration of the phenoxide, the

constant $a$ in the above equations is 0·002299, whereas by change of concentration of the iodide only, $a = 0·0009$, and, as was to be expected from these facts, the value of $a$ when the concentrations of both the phenoxide and the iodide were changed is equal to 0·002122, that is, lies between 0·002299 and 0·0009.

(3) The connexion between the velocity-coefficient and the initial concentration can be well expressed by the equation $K_v = K_1 + a\log v$, or by an equation of the type $K = p + q/c$.

### *General Conclusions.*

(1) The reaction between the alkyl iodides and sodium phenoxide in alcoholic solution is a bimolecular one of a special type, in which the velocity-coefficient varies with the initial concentration.

(2) The reactivities of the normal primary alkyl iodides with sodium phenoxide are in the following decreasing order of magnitude: methyl, ethyl, propyl, butyl, hexyl, heptyl, octyl, cetyl, and amyl iodides.

(3) The velocity-coefficients lie on a curve (with the exception of amyl iodide), which is very steep from methyl to butyl iodide, and is then very shallow, the velocity-coefficient of cetyl iodide not being much less than that of octyl iodide.

(4) In the cases of those iodides which have been previously investigated, the relative order of the reactivities found by the author agrees with that obtained by some other investigators, for example, Hecht, Conrad, and Bruckner (*loc. cit.*), who used sodium ethoxide, and Menschutkin, who employed triethylamine in acetone solution, but does not agree with that found by Burke and Donnan, whose reagent was silver nitrate.

(5) The relative reactivity of amyl iodide is unexpected. The velocity-coefficient of this substance has not previously been determined, and repeated measurements by the author confirm its comparative inactivity An explanation which might be suggested is that a cyclic compound is formed with the elimination of hydrogen iodide. It is interesting to notice that a parallel case was observed by Crocker (T., 1907, **91**, 593) in an investigation on the velocity of hydrolysis of the aliphatic amides, in which he found the velocity-constant of valeramide to be the smallest of the series.

The author desires to express his thanks to the Chemical Society Research Fund Committee for a grant, which has, in part, defrayed the cost of materials for this investigation.

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# CXXII.—*Rate of Evolution of Gases from Supersaturated Solutions. Part I. Influence of Colloids and of Suspensions of Charcoal on the Evolution of Carbon Dioxide.*

By ALEXANDER FINDLAY and GEORGE KING (Priestley Research Scholar, University of Birmingham).

IN the course of investigations of the influence of colloids on the solubility of gases (Findlay and Creighton, T., 1910, **97**, 536; Findlay and Shen, *ibid.*, 1912, **101**, 1459), marked differences were observed in the rate of escape of gas from supersaturated solutions. It was therefore deemed to be of interest to study the matter more fully, not only on account of the light which such investigations might throw on the properties of colloidal solutions, but also on account of its importance in connexion with biological problems (respiration, etc.) and industrial operations, such as the manufacture and the properties of mineral waters and other ærated beverages. In the present communication an account is given of the apparatus employed, the method of working, and the chief results so far obtained.

The problem of the rate of escape of gas from a supersaturated solution, and the factors which affect it, is one to which comparatively little attention has been given. Perman (T., 1895, **67**, 868; 1898, **73**, 511), by aspirating air through an aqueous solution of ammonia; Bohr (*Ann. Phys. Chem.*, 1899, [iii], **68**, 500), by passing air over the surface of an agitated aqueous solution of carbon dioxide; and Steele (T., 1903, **83**, 1470), by bubbling hydrogen through a solution of hydrogen chloride in toluene, found that the velocity with which the solutions were desaturated followed a logarithmic law; or the rate of desaturation was proportional to the concentration of the gas in the solution. By Carlson (*J. Chim. phys.*, 1911, **9**, 235) it has been found, more recently, that the logarithmic law is valid also for the rate of solution of oxygen and of carbon dioxide in water; and Bohr (*loc. cit.*) has shown that the ratio of the volume of gas which passes into solution through unit area in unit time (coefficient of invasion) to the volume of gas which similarly passes out of solution (coefficient of evasion) is constant, and equal to the absorption-coefficient.

It will be observed that the method of investigation employed hitherto is that of passing an indifferent gas through or over the solution, and the results obtained can, as has been pointed out by Meyer (*Zeitsch. Elektrochem.*, 1909, **15**, 249) and Carlson (*loc. cit.*), be interpreted in the light of the Nernst diffusion theory, which has proved so useful in connexion with heterogeneous solid–liquid systems (compare, however, Boselli, *J. Chim. phys.*, 1911, **9**, 689).

The method adopted by us, however, is essentially different, and is more in accordance with the conditions actually encountered. Moreover, the systems which we have investigated are, on account of the presence of colloids, very different from the simple aqueous solutions of a gas hitherto studied. Whether the method of aspirating an indifferent gas through such solutions would yield results of the same character as those which have been obtained by the method described later, will be investigated in the immediate future.

### *Apparatus and Method of Working.*

The apparatus employed, the outcome of the experience gained from a very large number of measurements, is represented diagrammatically in Fig. 1. The liquid from which the escape of gas is to be measured is contained in the solution-tube *A*, which is cylindrical in form, and is 25 cm. long and 3 cm. in diameter. To the ends of the tube are sealed two glass "trees," the purpose of which will be apparent later. Since it is necessary to employ in each experiment the same volume of solution, the tube *A* was calibrated, the volume being determined up to the mark *T* on the side-tube *Q*. This side-tube, which passes into the solution-tube at a point equidistant from the two ends, is connected by means of thick-walled rubber tubing and a mercury seal with a gas-measuring burette *M*. To prevent solution being carried by the escaping gas from the solution-tube to the mercury seal, a bulb trap and safety tube were blown on the side-tube *Q*. (The end of the safety tube was not as shown in the diagram, but was bent into the form of a loop.) About 10 cm. from one end of the solution-tube there is another side-tube *D*, furnished with a well-fitting capillary glass tap. The solution-tube, *A*, is held by rubber bands in a suitable frame, to which a spindle, carrying a cog-wheel, *X*, is attached. This spindle passed through a ball-bearing held firmly in a clamp, the whole being immersed, as indicated in the figure, in the water of a thermostat. The mercury seal and the burettes *K* and *M*, which were outside the thermostat, were water-jacketed.

The solution-tube, having been fixed in the frame so that the side-tube *Q* was co-linear with the spindle of the frame, could be caused to revolve by means of an electric motor and a driving chain * passing round the cog-wheel *X*. As the tube revolves, the rubber tubing attached to *Q* turns freely in a wide collar (not shown in the figure), and communicates the rotary movement along its whole length. It thus acts as a universal joint.* No difficulty

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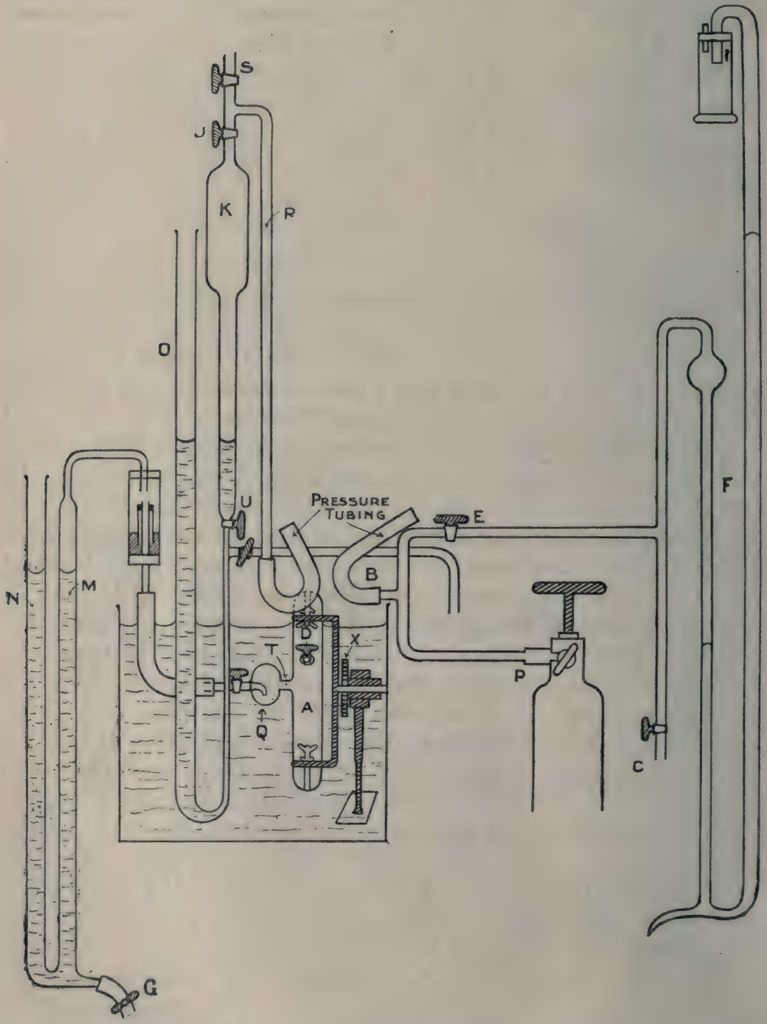
* It may be mentioned that it was found to be quite essential to employ a chain drive. By connecting the cogged driving wheel, the axle of which ran in ball-bearings, with the low gear of the motor by means of a stretched rubber band, it was found that instantaneous starting of the solution tube could be effected.

Fig. 1.



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* Although not absolutely necessary, owing to the rapidity with which the gas was evolved from the solutions, the precaution was adopted of coating the inside of the rubber tubing with a mixture composed of glycerol, glue, and water in the proportions 10 : 20 : 100, to prevent any diffusion of carbon dioxide through the rubber (*Gummi Zeit.*, 1912, **26**, 1626).

was found in obtaining satisfactory results with this joint, provided such care is taken in making the mercury seal as to ensure smooth running. We have found, also, that there is no detectable difference in the volume-reading in the burette *M* when the solution-tube is rotated or is at rest. Should any change occur, therefore, in the bore of the pressure tubing which constitutes the universal joint, owing to torsion, such change is too small to alter sensibly the volume of gas measured.

By the revolution of the solution-tube, *A*, also, the solution is caused to pass from end to end of the tube, and in so doing it falls on the glass "trees," and is thereby broken up. In this way a very efficient agitation of the solution is effected.

In carrying out an experiment, one proceeds as follows: The solution-tube, having been carefully cleaned and washed out with a quantity of the colloidal or other solution to be investigated, is finally filled with the latter to rather above the graduation mark. During the washing process care is taken to avoid the entrance of air into the apparatus by forcing the liquids out of the tube by means of carbon dioxide. When the tube and its contents have acquired the appropriate temperature, the volume of the solution is adjusted to the graduation mark, and a definite volume is then forced out of the solution-tube by means of carbon dioxide, the volume of liquid retained in the tube being, in all cases, 30·00 c.c.

The solution-tube having been placed in position in the thermostat, the liquid is saturated with carbon dioxide under a definite pressure (about 760 mm. above the prevailing atmospheric pressure) by connecting the side-tube *D* with the cylinder *P* containing the compressed gas. By means of the tap *E*, connexion is also established with a manometer *F*, whereby the gas pressure can be determined. Saturation of the solution with gas having been effected with agitation, the solution-tube is fixed upright in an automatically removable clamp, and allowed to remain undisturbed for some time. This period of repose is of great importance in order to ensure a period of quiescence on reducing the pressure. While the solution-tube is in the upright position, the portion projecting above the water of the thermostat is bathed in a stream of thermostat water which is kept in circulation by means of a Luther pump.

After thirty minutes the solution-tube is connected through the side-tube *D* and the tube *R* with the "reduction burette," *K*. This "reduction burette," which, together with the connecting tube *R* and the reservoir tube *O*, is enclosed in a water-jacket, contains, as measuring liquid, a solution of sodium hydrogen carbonate saturated with carbon dioxide. This solution is drawn up so as to fill the burette up to the tap *J*, which is then closed. The pressure in the tube *R* having been reduced to that of the atmosphere by opening and then closing the tap *S*, the taps *J* and *D* are opened, and communication thereby established between the solution-tube and the reduction burette. The gas in the solution-tube expands into the reduction burette, the negative pressure which obtains in the latter assisting the process. When the pressure in the reduction burette becomes equal to the atmospheric, the tap *D* is closed.* By opening the tap on the side-tube *Q*, any further gas was collected in the water-jacketed "measuring burette," *M*. This volume, together with that of the gas collected in the reduction burette, constitutes the "reduction volume," $V_R$.

In most cases it was found that escape of gas on reduction of the pressure to atmospheric was succeeded quite sharply by a period of quiescence during which no gas was evolved from the supersaturated solution. This period of quiescence, however, was obtained only when the solution was allowed to remain undisturbed for some time after saturation; for a period sufficiently long, in any case, to allow any froth, formed during saturation, to disappear. In certain cases, as will be described later, no quiescent period was obtained, and in the case of water the occurrence of a period of quiescence was somewhat irregular.

When the quiescent period set in, the burette reading was recorded, the solution-tube was unclamped and caused to revolve by starting the motor, and the rate of evolution of the gas from the supersaturated solution determined. As the gas passed over into the measuring burette, liquid was allowed to run out through the tube *G*, furnished with a spring clip, so that the pressure in the burette was always maintained equal to that of the atmosphere.

As the rate of escape of gas from the supersaturated solution was very great, it was found possible to measure it only by mechanical records on a rotating drum covered with smoked paper.† This drum was furnished with three writing points, actuated electromagnetically. One of these was connected with a clock beating half seconds, and so yielded a time line; a second point recorded the revolutions of the solution tube; whilst the third point was connected with a tapping key, by means of which a signal could be sent at certain definite volume-readings on the measuring burette.

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* The expulsion of the measuring liquid from the reduction burette was so rapid that there was no time for the liquid to drain from the walls. Accordingly, when atmospheric pressure had been established, the tap *U* was closed, and the volume reading taken after half an hour.

† Some idea of the velocity of evolution will be obtained when it is mentioned that in the case of concentrated gelatin solutions, 99·5 per cent. of the gas was evolved in 14·9 seconds, and during that time it was possible to obtain seventeen time-volume readings. It may also be stated that even with such rapid evolution of gas, volume readings could be made to 0·05 c.c.

### *Evolution of Carbon Dioxide from Unagitated Solutions.*

At the outset of this investigation a number of observations were made of the rate of escape of gas from unagitated supersaturated solutions. It has already been mentioned that on reducing the pressure of the gas above the solution to that of the atmosphere, a period of quiescence ensues, during which no gas escapes from the supersaturated solution. In this condition of metastability, however, the solution is exceedingly sensitive, a very slight mechanical shock being sufficient to cause a considerable evolution of gas. The occurrence of this period of quiescence is also prevented by even small traces of grease or dirt on the walls of the vessel, as well as by the presence of small particles of solid in the solution. Scrupulous care was therefore taken in the cleaning of the solution-tube.

The period of quiescence, however, did not persist indefinitely. After a shorter or longer time—in the case of certain gelatin solutions a period of twenty minutes was observed—a rather rapid spontaneous evolution of gas set in, which gradually diminished as the solution became desaturated. The diminution in the rate of escape of gas was, however, not continuous, but periodic, that is to say, the first rapid evolution gradually diminished to a certain extent when another comparatively rapid escape of gas took place. This was followed by an almost quiescent period, and at a certain point another comparatively rapid evolution of gas took place, and so on. This phenomenon, which does not seem to have been observed before, might perhaps be referred to changes in the surface layer of the liquid, but is probably to be explained more correctly as follows: Gas solutions, as has been known for long, readily remain supersaturated; that is to say, gaseous "nuclei" are formed with great difficulty. When, however, such nuclei are formed either in the body of the liquid or at the walls of the containing vessel, they will grow owing to diffusion into them of gas from the surrounding supersaturated solution. The bubbles attached to the walls of the vessel will, when they have acquired a certain size, detach themselves from the walls and escape. When these have escaped, nuclei again begin to be formed in the solution and on the walls of the vessel, and in the latter case they will, no doubt, be formed preferentially at the points where the bubbles were previously produced. These bubbles will increase in size as before, only more slowly as the solution becomes less concentrated, and the escape of this second series of bubbles, which, we may expect, will grow at about the same rate, and therefore detach themselves from the walls of the vessel at about the same time, will give rise to a second period of relatively rapid evolution, and so on. One would therefore expect that as the solution becomes less concentrated and the process of diffusion becomes slower, the length of the periods between the points at which the relatively rapid evolution of gas occurs would become longer. This is found, indeed, in some measure to be the case, but not completely so; and the reason for this may be that the diminution in the rate of growth of the bubbles which act as nuclei is more than counterbalanced by the formation of a larger number of nuclei.

Although the period of quiescence is well marked in the case of water, solutions of dextrin, and, more especially, solutions of gelatin, it is wanting in the case of solutions of peptone and ferric hydroxide. In these cases gas is evolved immediately when the pressure over the solution is reduced to that of the atmosphere. Although in the case of peptone solutions spontaneous evolution of gas sets in immediately, the rate of this spontaneous evolution is sufficiently slow to be measurable; but in the case of solutions of ferric hydroxide the rate of evolution is immeasurably rapid. After this first period of rapid evolution, however, the process goes on as in the case of the other solutions. It would therefore appear that in the case of solutions of ferric hydroxide there exists no essential difference as compared with other colloids, but that the metastable region with regard to gaseous supersaturation is much less. It may be that if the other solutions were supersaturated to a higher degree (by saturating with carbon dioxide at a higher pressure), there would also be no period of quiescence on reducing the pressure. We have not, however, investigated this.

The following figures will give an indication of the rate of evolution of carbon dioxide from unagitated water solutions:

| Time in minutes ...... | 1 | 3 | 7 | 14 | 24 |
|---|---|---|---|---|---|
| Volume in c.c. ......... | 0·5 | 1 | 1·5 | 2 | 2·5 |

The rate of evolution differed in the case of different solutions, but in most cases, after a period of about thirty minutes, it assumed an average value of about 1 c.c. in fourteen minutes, the time-volume curves then becoming parallel.

Although a number of experiments were carried out with unagitated solutions their study was abandoned, at least for the present, because quantitatively reproducible results could not be obtained.

### *Evolution of Carbon Dioxide from Agitated Supersaturated Solutions.*

As it was already well known from the work of others (Blanchard, *Zeitsch. physikal. Chem.*, 1902, **41**, 681; Walton, *ibid.*, 1904, **47**, 189; Lamplough, *Proc. Camb. Phil. Soc.*, 1908, **14**, 591) that gas supersaturation readily occurs in solution, and our own experiments having shown that no results of a sufficiently satisfactory or definite nature could be obtained with unagitated solutions, the apparatus previously described was devised to allow of the measurement of the evolution of gas from agitated solutions. With this apparatus a very large number of experiments have been carried out, and it has been found that results reproducible within narrow limits can be obtained.

For the purpose of obtaining an insight into the effect of various solutes or pseudo-solutes on the rate of evolution of gas, it is not sufficient merely to determine the volumes of gas evolved at given intervals of time, because of the fact that the total amount of gas evolved from equal volumes of solution has different values. The time-volume curves, therefore, although indicating differences in the case of different colloids, are not sufficiently distinctive, and cannot be compared directly with one another (see Fig. 2).

It has already been pointed out that Meyer (*loc. cit.*) has shown (on the basis of experiments by W. F. Knox) that the rate of removal of carbon dioxide from solution by a stream of air is proportional to the concentration of the carbon dioxide in the solution. If, in the cases studied by us, it is assumed that the rate of evolution is proportional to the degree of supersaturation, we obtain as the expression for the velocity of evolution, $\frac{dv}{dt}=k\left(1-\frac{v}{V}\right)$, where $v$ is the volume of gas evolved at time $t$ (in seconds) and $V$ the total volume evolved. The term $\left(1-\frac{v}{V}\right)$, therefore, represents the degree of supersaturation. On integration, this equation yields

$$k=\frac{2\cdot30}{t}.\log_{10}\left(1-\frac{v}{V}\right).$$

Here $k$ has a negative value, since the term $\left(1-\frac{v}{V}\right)$ is less than unity. Justification for the adoption of this equation as a basis on which comparison of the behaviour of different solutions can be instituted was found in the fact that in the case of the escape of gas from supersaturated solutions of carbon dioxide in pure water, the value of the coefficient $k$ is nearly constant. Moreover, the slight deviation from constancy which is found is proportional to the degree of supersaturation, so that when one plots the values of $k$ against the degree of supersaturation a straight line is obtained. By plotting the values of the velocity-coefficient against the degree of supersaturation in the case of different solutions, we have a means of representing clearly the distinctive and characteristic behaviour of colloids as affecting the escape of gas from supersaturated solution.

### *Method of Calculation.*

As is obvious, the expression given above is that of a unimolecular reaction; and if the rate of escape of gas from supersaturated solutions were strictly unimolecular, it would not matter from what stage of the evolution process the volume of gas were calculated. As a matter of fact, however, it is found that in the case of colloidal solutions the escape of gas is by no means a true unimolecular reaction; and even in the case of pure aqueous solutions a slight but definite trend in the value of $k$ is observable. It is necessary, therefore, to employ in the calculation of the velocity-coefficient values of $t_0$ and $v_0$ which shall be strictly comparable in the different cases. Unfortunately, it is not possible to employ the natural zero of time, namely, the moment at which evolution from the solution commences, on account of the time required (two to three seconds) to set up uniform agitation. This indefiniteness in the zero point is shown by the fact that none of the time-volume curves passes through the origin (Fig. 2). We have therefore selected as the zero time that point at which there remains in solution three-fourths of the theoretical amount of carbon dioxide in excess of that required to saturate the solution. This can be obtained from the solubility values determined by Findlay and Creighton and by Findlay and Shen. The value of $v_0$ having been calculated in this way, the corresponding time value can be obtained from the time-volume curve.

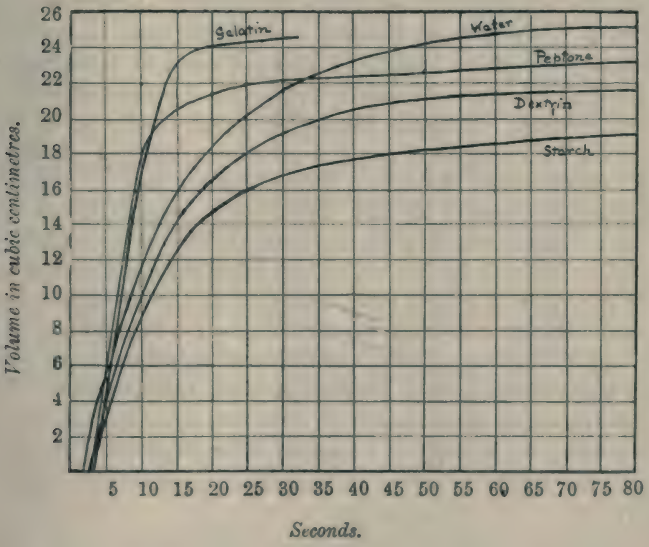
To give an indication of the accuracy of the experimental results we have given, at the head of each table, the total volume of gas evolved as actually measured ($V_e$) and as calculated from the solubility value ($V_t$), due regard being paid to the pressure of saturation and the pressure at which the gas was evolved. These pressures are represented by $B_s$, the barometric pressure at the time of saturation with gas; $B_e$, the barometric pressure at the time of evolution of gas; and $M$, the manometric pressure. $(M+B_s)$, therefore, represents the total pressure under which saturation with gas was carried out.

An example will render the method of calculation clearer. In the case of water (table I), for example, the solubility of carbon dioxide is 0·817. Since the volume of water in the solution-tube is 30·0 c.c. (p. 1173), we can imagine that the water is removed, and that we are dealing with carbon dioxide contained in an actual volume of $30{\cdot}0\times0{\cdot}817=24{\cdot}51$ c.c. When saturation of the solution takes place, we can imagine that carbon dioxide is compressed into the volume of 24·51 c.c. under a pressure of $(M+B_s)=1493{\cdot}1$ mm. On reducing the pressure to $B_e=745{\cdot}0$ mm., and allowing carbon dioxide to escape, the volume which escapes should be, theoretically:

$$V_t=\frac{24{\cdot}51\times1493{\cdot}1}{745{\cdot}0}-24{\cdot}51=24{\cdot}60.$$

To obtain the zero volume on the "three-fourths basis" referred to above, we have $v_0=(V_e-\frac{3}{4}V_t)$. Hence, again taking the data from table I, we obtain $v_0=24{\cdot}55-18{\cdot}46=6{\cdot}09$. From the time-volume curve, one obtains the corresponding time value $t_0=7{\cdot}5$. The corrected values of time and volume are then obtained by subtracting 7·5 secs. from the direct time readings, and 6·09 c.c. from the corresponding volume readings.

FIG. 2.



The correctness of the observed volume of gas evolved can be checked, not only by comparing the values of $V_e$ and $V_t$ (which can be done when the quiescent period is well marked), but also by measuring the "reduction volume" $V_R$. If the gas space in the solution tube is represented by $V_G$, the correct "reduction volume," or the volume of gas which should escape from the solution-tube, owing to the expansion of the compressed gas, should be:

$$V_{RC} = \frac{V_G \times M + B_s}{B_e} - V_G = V_G \frac{M + B_s - B_e}{B_e}.$$

By comparing the value of $(V_e + V_R)$ with $(V_t + V_{RC})$, the correctness of the total volume reading can be checked. Thus, from the data in table I, we have $(V_e + V_R) = (24{\cdot}55 + 127{\cdot}9) = 152{\cdot}45$; and $(V_t + V_{RC}) = (24{\cdot}6 + 128{\cdot}2) = 152{\cdot}8$. This check is especially useful when there is no distinct quiescent period. In those cases where the solubility varies with the pressure, due regard must be paid to the fact in making the calculations.

## Experimental.

In all the experiments recorded here the temperature employed was 25·0°. The carbon dioxide was taken from a cylinder of commercial gas, which contained 0·33 per cent. of impurity, a fact which must be borne in mind when one employs the solubility data for the gas. It ought also to be stated that it is of essential importance to work with air-free solutions, and to expel all air from all the tubes of the apparatus. Another factor of the utmost importance is time. In the case more especially of gelatin and starch solutions, the time taken in the preparation of the solutions, the period during which the solutions remained in contact with the carbon dioxide, etc., were found to exercise a marked effect on the slope of the curve obtained. The whole series of operations in connexion with the different solutions were therefore carried out according to a very strict time table. When this was done, and all other conditions kept constant, velocity-supersaturation curves exactly reproducible as regards their slope could be obtained, although the absolute values of the velocity-coefficients might vary slightly.

With regard to the rotation of the solution-tube, the speed of 20 revolutions per minute was chosen as giving a velocity of evolution of gas which is measurable and reproducible. The influence of the speed of rotation is, however, not very great, and the variations which occurred in the course of the work are negligible in this respect. The speed of rotation is given at the head of each table, and is represented by $R$.

### 1. *Water.*

A very large number of experiments (more than 120) have been carried out with solutions of carbon dioxide in water; and the following results may be taken as typical of all. In this table we have also given the corrected times and volumes, that is, the times and volumes as measured from the value of $t_0$ and $v_0$.

TABLE I.

$M$=748·2 mm. $V_e$=24·55 $V_R$=127·9 $t_0$=7·5
$B_s$=744·9 $V_t$=24·60 $V_{RC}$=128·2 $v_0$=6·09
$B_e$=745·0 Solubility=0·817 $R$=18·7

| Time. | Volume. | Corrected time. | Corrected volume. | Super-saturation. | $-k$. |
|---|---|---|---|---|---|
| 5·1 | 3·1 | — | — | — | — |
| 6·7 | 5·1 | — | — | — | — |
| 8·35 | 7·1 | 0·85 | 1·01 | 0·945 | 0·0666 |
| 10·15 | 9·1 | 2·65 | 3·01 | 0·837 | 0·0672 |
| 13·35 | 12·1 | 5·85 | 6·01 | 0·674 | 0·0673 |
| 14·65 | 13·1 | 7·15 | 7·01 | 0·620 | 0·0668 |
| 17·80 | 15·1 | 10·3 | 9·01 | 0·512 | 0·0650 |
| 21·55 | 17·1 | 14·05 | 11·01 | 0·404 | 0·0646 |
| 26·65 | 19·1 | 19·15 | 13·01 | 0·295 | 0·0637 |
| 34·20 | 21·1 | 26·7 | 15·01 | 0·185 | 0·0632 |
| 55·80 | 23·6 | 48·3 | 17·51 | 0·051 | 0·0614 |
| ∞ | 24·55 | ∞ | 18·46 | — | — |

### 2. *Solutions of Potassium Chloride.*

The velocity of evolution of carbon dioxide from solutions of potassium chloride of various concentrations has been investigated, and the following table reproduces the results obtained with the most concentrated solution.

TABLE II.

Concentration: 60·00 grams of potassium chloride in 1 litre of solution.

$M$=761·0 mm. $V_e$=22·60 $V_R$ =127·7 $t_0$= 7·35
$B_s$=759·0 $V_t$=22·58 $V_{RC}$=127·9 $v_0$= 5·66
$B_e$=759·0 Solubility=0·765 $R$=20·3

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 3·9 | 2·8 | — | — |
| 5·1 | 3·8 | — | — |
| 7·4 | 5·8 | 0·918 | 0·0615 |
| 10·9 | 8·8 | 0·815 | 0·0576 |
| 13·8 | 10·8 | 0·697 | 0·0561 |
| 15·3 | 11·8 | 0·637 | 0·0566 |
| 21·3 | 14·8 | 0·461 | 0·0555 |
| 31·6 | 17·8 | 0·285 | 0·0518 |
| 43·6 | 19·8 | 0·167 | 0·0494 |
| 53·1 | 20·8 | 0·107 | 0·0487 |

*Colloidal Solutions.*—The rate of evolution of carbon dioxide from solutions containing colloids was also determined. Before use, the solutions were filtered through a Hirsch funnel in order to eliminate the effect of solid particles on the velocity of evolution (Veley. *Phil. Trans.*, 1888, *A*, **179**, 264).

### 3. *Solutions of Gelatin.*

For these experiments Coignet's Gold Medal French gelatin was used. It was found to be very free from insoluble matter.

### TABLE III (compare Fig. 3).

Concentration: 0·242 gram of gelatin in 1 litre of solution.

$M=760{\cdot}2$ mm. $V_e=25{\cdot}5$ $V_R=130{\cdot}0$ $t_0=7{\cdot}75$
$B_s=742{\cdot}5$ $V_t=25{\cdot}13$ $V_{RC}=130{\cdot}9$ $v_0=6{\cdot}65$
$B_e=742{\cdot}1$ Solubility $=0{\cdot}817$ $R=20$

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 3·5 | 1·6 | — | — |
| 5·4 | 3·6 | — | — |
| 6·1 | 4·6 | — | — |
| 7·7 | 6·6 | — | — |
| 11·6 | 11·6 | 0·738 | 0·0791 |
| 13·3 | 13·6 | 0·631 | 0·0829 |
| 15·3 | 15·6 | 0·525 | 0·0852 |
| 16·3 | 16·6 | 0·472 | 0·0877 |
| 17·4 | 17·6 | 0·419 | 0·0901 |
| 18·7 | 18·6 | 0·366 | 0·0917 |
| 20·0 | 19·6 | 0·313 | 0·0948 |
| 23·6 | 21·6 | 0·207 | 0·0994 |
| 26·0 | 22·6 | 0·154 | 0·1025 |

### TABLE IV (compare Fig. 3).

Concentration: 0·281 gram of gelatin in 1 litre of solution.

$M=755{\cdot}3$ mm. $V_e=25{\cdot}0$ $V_R=128{\cdot}5$ $t_0=7{\cdot}35$
$B_s=746{\cdot}9$ $V_t=24{\cdot}78$ $V_{RC}=128{\cdot}6$ $v_0=6{\cdot}41$
$B_e=747{\cdot}1$ Solubility $=0{\cdot}817$ $R=20{\cdot}5$

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 2·95 | 1·0 | — | — |
| 5·1 | 3·0 | — | — |
| 5·8 | 4·0 | — | — |
| 7·1 | 6·0 | — | — |
| 8·9 | 8·8 | 0·872 | 0·0891 |
| 10·25 | 11·0 | 0·753 | 0·0977 |
| 11·4 | 13·0 | 0·646 | 0·1079 |
| 13·5 | 16·0 | 0·484 | 0·1178 |
| 15·1 | 18·0 | 0·377 | 0·1258 |
| 16·0 | 19·0 | 0·322 | 0·1309 |
| 19·85 | 22·0 | 0·161 | 0·1459 |
| 22·1 | 23·0 | 0·108 | 0·1510 |
| 26·2 | 24·0 | 0·054 | 0·1549 |

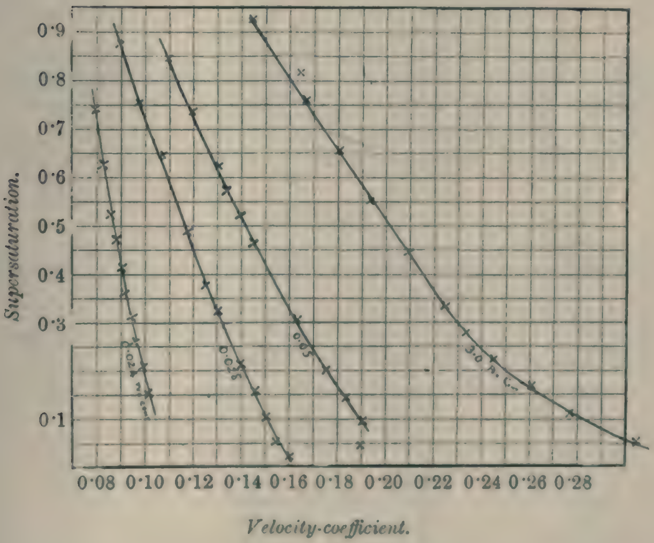
### TABLE V (compare Fig. 3).

Concentration: 0·502 gram of gelatin in 1 litre of solution.

| | | | |
|---|---|---|---|
| $M = 759{\cdot}5$ mm. | $V_e = 24{\cdot}25$ | $V_R = 129{\cdot}1$ | $t_0 = 6{\cdot}55$ |
| $B_s = 747{\cdot}6$ | $V_t = 24{\cdot}90$ | $V_{RC} = 129{\cdot}7$ | $v_0 = 5{\cdot}57$ |
| $B_e = 747{\cdot}6$ | Solubility $= 0{\cdot}817$ | | $R = 19{\cdot}3$ |

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 4·7 | 2·5 | — | — |
| 6·0 | 4·5 | — | — |
| 6·5 | 5·5 | — | — |
| 8·1 | 8·5 | 0·843 | 0·1099 |
| 9·1 | 10·5 | 0·736 | 0·1199 |
| 10·1 | 12·5 | 0·629 | 0·1305 |
| 10·7 | 13·5 | 0·576 | 0·1328 |
| 11·8 | 15·5 | 0·469 | 0·1443 |
| 13·8 | 18·5 | 0·308 | 0·1623 |
| 15 7 | 20·5 | 0·201 | 0·1752 |
| 19·0 | 22·5 | 0·094 | 0·1900 |
| 23·5 | 23·5 | 0·040 | 0·1893 |

FIG. 3.



### TABLE VI (compare Fig. 3).

Concentration: 30·01 grams of gelatin in 1 litre of solution.

$M=759{\cdot}2$ mm. $V_e=24{\cdot}4$ $V_R=128{\cdot}8$ $t_0=5{\cdot}7$
$B_s=755{\cdot}1$ $V_t=24{\cdot}51$ $V_{RC}=128{\cdot}6$ $v_0=6{\cdot}02$
$B_e=755{\cdot}0$ Solubility$=0{\cdot}825$ and $0{\cdot}819$ at $B_e$ and at $(M+B_s)$
$R=22$ respectively

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 4·0 | 2·3 | — | — |
| 5·0 | 4·3 | — | — |
| 5·4 | 5·3 | — | — |
| 6·2 | 7·3 | 0·930 | 0·1440 |
| 6·9 | 9·3 | 0·822 | 0·1639 |
| 7·3 | 10·3 | 0·767 | 0·1656 |
| 8·4 | 12·3 | 0·658 | 0·1816 |
| 9·6 | 16·3 | 0·441 | 0·2098 |
| 10·6 | 18·3 | 0·332 | 0·2249 |
| 11·8 | 20·3 | 0·223 | 0·2453 |
| 12·5 | 21·3 | 0·170 | 0·2615 |
| 13·5 | 22·3 | 0·115 | 0·2771 |
| 14·9 | 23·3 | 0·060 | 0·3050 |
| 19·0 | 24·3 | 0·006 | 0·3904 |

### 4. *Solutions of Dextrin.*

Kahlbaum's pure dextrin was employed, and a large number of readings were recorded with varying concentrations. The following are selected as representative.

### TABLE VII.

Concentration: 10·0 grams of dextrin in 1 litre of solution.

$M=756{\cdot}6$ mm. $V_e=23{\cdot}9$ $V_R=125{\cdot}9$ $t_0=6{\cdot}7$
$B_s=767{\cdot}5$ $V_t=24{\cdot}49$ $V_{RC}=125{\cdot}9$ $v_0=5{\cdot}53$
$B_e=767{\cdot}3$ Solubility$=0{\cdot}812$ $R=22$

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 4·6 | 3·0 | — | — |
| 6·2 | 5·0 | — | — |
| 7·0 | 6·0 | — | — |
| 8·8 | 8·0 | 0·867 | 0·0687 |
| 10·8 | 10·0 | 0·757 | 0·0679 |
| 11·7 | 11·0 | 0·702 | 0·0707 |
| 14·2 | 13·0 | 0·594 | 0·0694 |
| 17·2 | 15·0 | 0·485 | 0·0689 |
| 21·4 | 17·0 | 0·376 | 0·0665 |
| 27·0 | 19·0 | 0·267 | 0·0593 |
| 76·3 | 23·5 | 0·022 | 0·0548 |

### TABLE VIII.

Concentration: 30·0 grams of dextrin in 1 litre of solution.

$M$ = 763·4 mm. $V_e$ = 24·55 $V_R$ = 130·4 $t_0$ = 7·0
$B_s$ = 744·8 $V_t$ = 24·95 $V_{RC}$ = 131·1 $v_0$ = 5·84
$B_e$ = 744·0 Solubility = 0·804 and 0·801 at the pressures of
$R$ = 21·4 saturation and evolution

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 5·1 | 3·5 | — | — |
| 5·8 | 4·5 | — | — |
| 9·3 | 8·5 | 0·858 | 0·0666 |
| 12·4 | 11·5 | 0·697 | 0·0667 |
| 13·5 | 12·5 | 0·644 | 0·0676 |
| 16·9 | 14·5 | 0·537 | 0·0627 |
| 21·6 | 16·5 | 0·430 | 0·0577 |
| 28·2 | 18·5 | 0·323 | 0·0533 |
| 33·3 | 19·5 | 0·270 | 0·0498 |
| 39·9 | 20·5 | 0·216 | 0·0466 |
| 44·8 | 21·0 | 0·190 | 0·0439 |

### TABLE IX.

Concentration: 125·1 grams of dextrin in 1 litre of solution.

$M$ = 759·6 mm. $V_e$ = 23·2 $V_R$ = 130·1 $t_0$ = 6·85
$B_s$ = 741·1 $V_t$ = 23·37 $V_{RC}$ = 130·9 $v_0$ = 5·67
$B_e$ = 741·1 Solubility = 0·753 and 0·746 at saturation and
$R$ = 21·0 at evolution pressures respectively

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 4·1 | 2·0 | — | — |
| 5·6 | 4·0 | — | — |
| 6·4 | 5·0 | — | — |
| 7·8 | 7·0 | 0·924 | 0·0829 |
| 9·3 | 9·0 | 0·810 | 0·0828 |
| 13·4 | 13·0 | 0·582 | 0·0824 |
| 15·0 | 14·0 | 0·525 | 0·0789 |
| 19·0 | 16·0 | 0·411 | 0·0732 |
| 25·3 | 18·0 | 0·297 | 0·0658 |
| 30·2 | 19·0 | 0·240 | 0·0612 |
| 40·4 | 20·5 | 0·154 | 0·0557 |
| 61·7 | 22·0 | 0·069 | 0·0488 |
| 118·0 | 23·0 | 0·011 | 0·0402 |

### 5. *Solutions of Starch.*

Kahlbaum's soluble starch was employed. As it was found that the form of the curve for the velocity-coefficient against supersaturation depends on the history of the solution, the results of only one series of measurements are communicated, a fuller investigation of the behaviour of starch solutions being reserved for a future time.

TABLE X (compare Fig. 4).

Concentration: 30·0 grams of starch in 1 litre of solution.

$M$=753·0 mm. $V_e$=23·75 $V_R$ =128·3 $t_0$=7·0
$B_s$=747·7 $V_t$=24·79 $V_{RC}$=128·7 $v_0$=5·2
$B_e$=747·5 Solubility=0·806 and 0·700 at saturation and
$R$= 21 at evolution pressures respectively

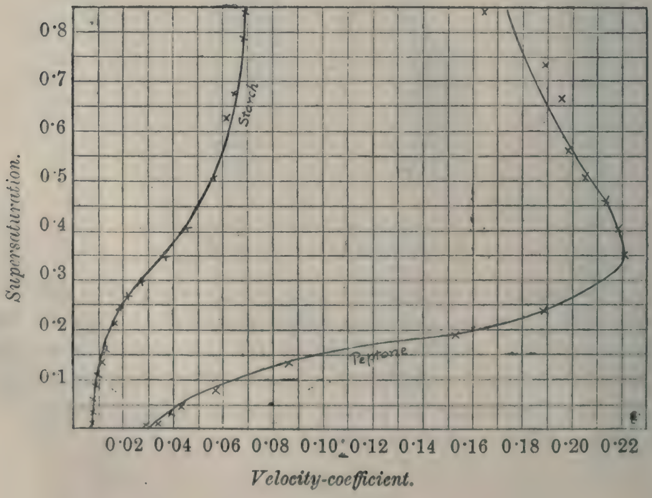
| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 3·2 | 1·2 | — | — |
| 5·3 | 3·2 | — | — |
| 6·1 | 4·2 | — | — |
| 7·9 | 6·2 | — | — |
| 9·6 | 8·2 | 0·837 | 0·0686 |
| 10·6 | 9·2 | 0·783 | 0·0680 |
| 13·1 | 11·2 | 0·675 | 0·0643 |
| 16·5 | 13·2 | 0·568 | 0·0596 |
| 22·0 | 15·2 | 0·460 | 0·0517 |
| 35·8 | 17·2 | 0·352 | 0·0362 |
| 82·0 | 19·2 | 0·245 | 0·0188 |
| 132·0 | 20·3 | 0·186 | 0·0134 |
| 252·0 | 21·8 | 0·105 | 0·0093 |
| 392·0 | 22·6 | 0·062 | 0·0072 |
| 587·0 | 23·4 | 0·019 | 0·0068 |

### 6. *Solutions of Peptone.*

In these experiments commercial peptone (Witte's peptone) was used. It consists largely of albumoses (Mann, *Chemistry of Proteids*, p. 179), and contains a considerable quantity of insoluble material.

Since the form of curve is very different from that obtained with

FIG. 4.



other solutions, we propose to study these solutions more fully at a later date. Solutions of only one concentration of peptone have been investigated, but the form of the curve has been confirmed by three distinct experiments. As has already been mentioned, solutions of peptone exhibit no well-defined quiescent period, and they are further distinguished from the solutions previously described by the fact that there is a much greater production of froth.

As the value of the solubility of carbon dioxide given by Findlay and Shen refers to pure carbon dioxide, we have used a proportionately lower value for the commercial carbon dioxide employed by us.

TABLE XI (compare Fig. 4).

Concentration: 7·58 grams of peptone in 1 litre of solution.

$M=753{\cdot}9$ mm. $V_e=23{\cdot}5$ $V_R=127{\cdot}5$ $t_0=4{\cdot}05$
$B_s=760{\cdot}9$ $V_t=24{\cdot}43$ $V_{RC}=126{\cdot}9$ $v_0=5{\cdot}2$
$B_e=760{\cdot}5$ Solubility = 0·838 and 0·855 $R=20$

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 3·3 | 3·1 | — | — |
| 4·0 | 5·1 | — | — |
| 4·35 | 6·1 | — | — |
| 5·1 | 8·1 | 0·842 | 0·164 |
| 5·7 | 10·1 | 0·732 | 0·189 |
| 6·1 | 11·1 | 0·671 | 0·195 |
| 6·9 | 13·1 | 0·568 | 0·195 |
| 7·3 | 14·1 | 0·514 | 0·205 |
| 7·7 | 15·1 | 0·459 | 0·213 |
| 8·8 | 17·1 | 0·350 | 0·221 |
| 11·6 | 19·1 | 0·241 | 0·189 |
| 27·7 | 21·1 | 0·131 | 0·086 |
| 74·0 | 22·6 | 0·049 | 0·043 |
| 155·0 | 23·3 | 0·011 | 0·028 |

### 7. *Solutions of Ferric Hydroxide.*

As has already been mentioned, solutions of ferric hydroxide supersaturated with carbon dioxide show no quiescent period on reducing the pressure. After a period of rapid evolution, however, the solutions become quiet although still supersaturated to some extent. These solutions were then shaken, and the velocity-coefficient of gas evolution was determined, zero time being taken as the moment when agitation was commenced. As we are here dealing with solutions from which a great portion of the dissolved gas has already escaped, the values of the velocity-coefficient are not strictly comparable with those obtained in the previous cases. In the following tables we have calculated the velocity-coefficient on the basis of the total volume of gas evolved after the first rush of gas had ceased and quiescence had set in.

### TABLE XII.

Concentration: 13·53 grams of ferric hydroxide in 1 litre of solution.

$M=758$ mm. $B=762$ $V_e=9·5$ $R=20·3$

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 3·5 | 2·0 | 0·790 | 0·067 |
| 5·3 | 3·0 | 0·685 | 0·072 |
| 8·6 | 4·5 | 0·527 | 0·074 |
| 12·5 | 5·5 | 0·422 | 0·069 |
| 15·1 | 6·0 | 0·369 | 0·066 |
| 20·6 | 7·0 | 0·264 | 0·064 |
| 31·8 | 8·0 | 0·158 | 0·058 |

### TABLE XIII.

Concentration: 3·767 grams of ferric hydroxide in 1 litre of solution.

$M=763·2$ mm. $B=755·5$ $V_e=14·6$ $R=20$

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 5·6 | 3·4 | 0·767 | 0·047 |
| 6·4 | 3·9 | 0·733 | 0·048 |
| 7·6 | 4·9 | 0·665 | 0·054 |
| 9·1 | 5·9 | 0·596 | 0·057 |
| 9·8 | 6·4 | 0·561 | 0·063 |
| 13·2 | 8·4 | 0·425 | 0·065 |
| 15·5 | 9·4 | 0·356 | 0·067 |
| 19·7 | 10·9 | 0·256 | 0·069 |
| 23·4 | 11·9 | 0·187 | 0·072 |
| 29·4 | 12·9 | 0·117 | 0·073 |

## 8. *Colloidal Solutions of Platinum.*

The escape of carbon dioxide from colloidal solutions of platinum, prepared by Bredig's method, showed practically no difference as compared with the escape from pure water.

## 9. *Solutions of Agar.*

For the purpose of comparison with solutions of gelatin, one experiment was carried out with a solution of agar, the concentration of the latter being 1·522 grams in 1 litre of solution. As the solubility of carbon dioxide in solutions of agar is not recorded, the values of $k$ were calculated solely from the volumes of gas evolved, measured from the moment when shaking commenced. In the following table we give, for the sake of shortness, only the values of supersaturation and the calculated value of the coefficient.

### TABLE XIV.

| | | | | | | |
|---|---|---|---|---|---|---|
| Supersaturation ...... | 0·76 | 0·66 | 0·46 | 0·27 | 0·12 | 0·023 |
| $-k$ .................... | 0·033 | 0·039 | 0·050 | 0·054 | 0·065 | 0·072 |

### 10. *Suspensions of Charcoal.*

A fine suspension of Kahlbaum's bone charcoal was employed. When the saturation with carbon dioxide was carried out, as in the previous experiments, by allowing the carbon dioxide to remain in contact with the suspension for an hour and a-half, a curve resembling that for pure water was obtained. If, however, the saturation was prolonged over a period of forty-eight hours, the results given in the following table were obtained. Since, in this experiment, the total volume of gas evolved did not equal that calculated from the solubility data of Findlay and Creighton, the values of $k$ were calculated from the actual volumes measured. The zero of time was again calculated from the point at which the degree of supersaturation was 0·75 on the basis of the total volume of gas evolved.

TABLE XV.

| Time. | Volume. | Supersaturation. | $-k$. |
|---|---|---|---|
| 13·8 | 9·4 | 0·80 | 0·042 |
| 15·5 | 10·4 | 0·75 | 0·042 |
| 19·5 | 12·4 | 0·63 | 0·042 |
| 25·4 | 14·4 | 0·52 | 0·039 |
| 29·0 | 15·4 | 0·46 | 0·039 |
| 36·9 | 16·9 | 0·38 | 0·034 |
| 63·9 | 18·9 | 0·27 | 0·024 |
| 102·0 | 19·9 | 0·21 | 0·017 |
| 155·4 | 20·5 | 0·18 | 0·012 |
| 252·0 | 21·5 | 0·12 | 0·009 |
| 367·0 | 22·3 | 0·07 | 0·007 |
| 827·0 | 23·3 | 0·02 | 0·005 |

### *Discussion of Results.*

A consideration of the results communicated in the preceding pages will show that in the case of unagitated solutions, supersaturation can occur to a very marked extent, solutions of gelatin, especially, which had been saturated at a pressure of about two atmospheres, remainng quite quiescent and evolving no gas when the pressure was reduced to one atmosphere. As mentioned, however, this period of quiescence is one during which the solution is in a very sensitive metastable state, and this may perhaps account for the fact that in connexion with the velocity of certain reactions as studied by the amount of gas evolved, considerable discussion has been evoked with regard to the importance of shaking the solutions (Lamplough, *loc. cit.*; Veley, *Trans. Faraday Soc.*, 1909, **5**, 1). Our experiments certainly show that with carefully cleaned apparatus and in the absence of mechanical shock, supersaturation can occur to a very marked extent.

With regard to the escape of gases from agitated solutions, our experiments show that the rate of escape of carbon dioxide from pure supersaturated aqueous solutions, is very nearly proportional to the degree of supersaturation. In all cases, however, the value of the velocity-coefficient was found to diminish to a slight extent as the supersaturation diminished; and this diminution appears to be an essential, and not merely a chance phenomenon, as it was found even with different apparatus, and was in all cases practically the same in amount.

As long ago as 1869, it was observed by H. Müller (T., 1870, **23**, 37), in connexion with the manufacture of soda-water, that "in order to make the water take up carbonic acid gas in such a manner that the gas may not be immediately disengaged when the liquid is let out of the apparatus, it is necessary that the gas and water be left together in the apparatus for at least twenty-four hours. If the agitation is continued merely for an hour or an hour and a-half, then, on letting out the water, the carbonic anhydride instantly disengages itself, the water becomes creamy, the gas comes up immediately, and the effervescence is over; whereas, if the gas be allowed to remain in contact with the water from twenty to twenty-four hours, and the liquid be then let out, the carbonic anhydride disengages itself from the water gradually, and attaches itself to the sides of the glass, seeming, indeed, to be altogether in a different state to that in which it is, after being left for only a short time in contact with the water. It appears, indeed, that in one case, that is, after a short contact, the carbonic anhydride dissolves in the water merely as such, but that after prolonged contact it becomes hydrated, and is dissolved by the water as hydrogen carbonate, or carbonic acid, and is then retained more firmly." We have not been able to obtain any confirmation of such a difference, no variation in the velocity of evolution of carbon dioxide having been observed, although the period of saturation with carbon dioxide under pressure varied from about an hour and a half up to three weeks. The explanation of the behaviour observed by Müller is most probably to be found in the presence of grease or other matter on the walls of the glass or of solid particles suspended in the liquid. These materials retain minute quantities of air, which then acts as a "nucleus," and brings about the evolution of the carbon dioxide from the supersaturated solution. When the process of saturation is continued for a lengthened period, the air retained by the solid particles will get dissolved, and there will consequently be no "nuclei" to initiate the evolution of the carbon dioxide. The very important effect of even traces of grease in overcoming supersaturation has been observed by a number of investigators, as well as most distinctly by our ourselves. Most scrupulous care in cleaning the solution-tube had to be exercised, if a distinct quiescent period was to be obtained.

The phenomenon of the escape of gas from supersaturated aqueous solution is a comparatively simple one; and so also does it appear to be in the case of solutions of electrolytes, such as potassium chloride, which appear to have no influence, or practically none, on the rate of evolution of carbon dioxide from supersaturated solution. Quite otherwise is it, however, when colloids are present in solution. In this case the phenomenon becomes much more complicated, and considerable differences are found in the case of the different colloidal solutions.

Even the direct time-volume curves (Fig. 2) show that there is a marked difference in the behaviour of different colloids. Thus, in the case of solutions of gelatin, peptone, ferric hydroxide, and agar, there is a much more rapid evolution of gas initially than is found in the case of water, and solutions of potassium chloride, dextrin, or starch. The differences are, however, more obvious when one considers the velocity-coefficient–supersaturation curves and tables. From these one sees that dextrin has not a very marked influence on the rate of escape even when the concentration of the dextrin is 3 per cent. It is noticeable, however, that there is a marked diminution of the velocity-coefficient as the degree of supersaturation diminishes. This behaviour is not characteristic of dextrin, however, but it found also in the case of other colloids; starch shows it very conspicuously as well as the ferric hydroxide solution of 0·38 per cent. concentration. In the case of suspensions of charcoal, a similar very marked diminution of the velocity-coefficient is observed in those cases, and only in those cases where the suspension was kept in contact with the carbon dioxide for a lengthened period. We are led by this behaviour on the part of charcoal to think of the relatively slow rate of absorption of carbon dioxide by charcoal which follows on the period of comparatively rapid absorption (Findlay and Creighton, *loc. cit.*), and to explain the falling off in the value of the velocity-coefficient to a slow outward diffusion of the carbon dioxide dissolved in the charcoal. Whether this should prove to be a true explanation or not, it is noteworthy that in the case of starch also, Findlay and Creighton found that saturation with carbon dioxide takes place more slowly than in the case of other colloids studied by them.

A markedly different behaviour is found in the case of solutions of gelatin and of agar, the former having been most fully investigated. In these cases the velocity-coefficient increases with diminution in the supersaturation, and the more so the greater the concentration of the gelatin.

Still more conspicuous in its behaviour is peptone. In this case, as, more pronouncedly, in the case of ferric hydroxide, there was no quiescent period on releasing the pressure of gas above the supersaturated solution. There is a comparatively rapid evolution of carbon dioxide until the supersaturation has diminished to about half, and then the velocity-coefficient rapidly falls away, owing to the very slow rate at which the gas is evolved. As the peptone used by us has been shown to consist largely of albumoses, its behaviour is of interest from the point of view of the manufacture and the palatability of aerated beverages, since beers contain appreciable amounts of albumoses. Their effect would therefore be to delay the occurrence of "flatness" in the beer.

There is, however, one property to which casual reference only has been made, but which exercises an important influence on the rate of escape of gas from solutions of gelatin and of starch; that is, the change which was found to take place in gelatin and starch solutions on being kept in contact with carbon dioxide for varying periods of time, or on being repeatedly re-saturated with carbon dioxide. In such cases, the characteristic influence of the gelatin and starch disappeared, and the behaviour approached to that with pure water. This question of ageing is one of great importance, and we hope to investigate and report on this matter more fully at a later time.

For the varied behaviour of the different colloids, no explanation can as yet be offered. One is, of course, inclined at first to try to bring the process of evolution into relation with the viscosity and surface tension of the solutions; and, certainly, one would be inclined to expect that these properties would exercise some influence on the behaviour of the solutions. The rapid evolution from peptone solutions, for example, might be referred to the diminished surface tension; but the difficulty would still remain, that the last third of the gas escapes with great slowness. The question, however, merits fuller investigation, and we hope to determine the viscosity and surface tension of the solutions we have used both before and after saturation with carbon dioxide. Meanwhile we offer the report on the experiments we have so far carried out as a first contribution to the study of a very complex problem.

The experimental work described in this paper was carried out in the Chemistry Department of the University of Birmingham, and we are indebted to Prof. Frankland for the many facilities which he placed at our disposal.

CHEMICAL DEPARTMENT,
UNIVERSITY OF BIRMINGHAM.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

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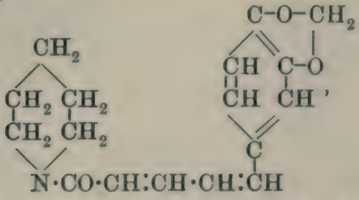
## CXXIII.—*The Relation between the Absorption Spectra and Constitution of Piperine, Nicotine, Cocaine, Atropine, Hyoscyamine, and Hyoscine.*

By JAMES JOHNSTON DOBBIE and JOHN JACOB FOX.

IN recent papers (T., 1911, **99**, 1254; 1912, **101**, 77) it was shown that each of the alkaloids cinchonine, quinine, and cupreine gives an absorption spectrum which is almost identical with the spectrum of that part of the molecule of the alkaloid which is unreduced; quinoline in the case of cinchonine, 6-methoxy- and 6-hydroxy-quinoline in the cases of quinine and cupreine respectively.

We have obtained similar results with other alkaloids of known constitution, in which a reduced is combined with an unreduced nucleus. The alkaloids examined in this connexion were piperine, nicotine, cocaine, and atropine, which, as will be seen from the figure, give spectra differing widely from one another.

The alkaloid piperine:

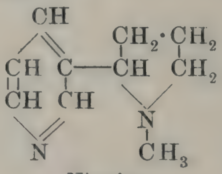


contains piperidine in combination with the piperic acid residue, and, under the influence of hydrolytic agents, yields piperidine and piperic acid:

$$\underset{\text{Piperine.}}{C_{17}H_{19}O_3N} + H_2O = \underset{\text{Piperidine.}}{C_5H_{11}N} + \underset{\text{Piperic acid.}}{C_{12}H_{10}O_4}$$

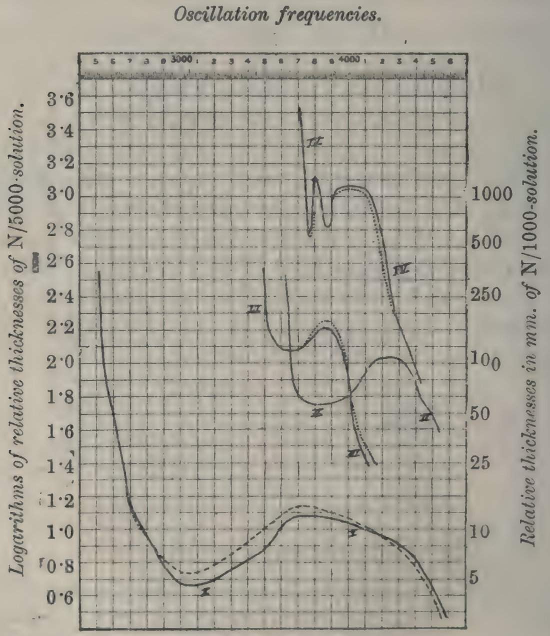
Piperidine is a completely reduced substance, and its alcoholic solution gives no absorption bands. Piperic acid, on the other hand, contains an unreduced benzene nucleus; its spectrum exhibits strong absorption, and contains a wide absorption band the head of which lies at 1/λ 3070. On comparing the absorption curve of piperic acid with that of piperine, the two are seen to be almost identical.

Nicotine has a pyridine ring united with a methylpyrrolidine which is completely reduced.



Nicotine.

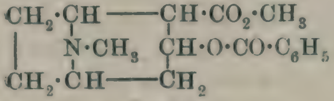
The curve of the absorption spectrum of nicotine closely resembles that of the picolines (Baly and Baker, T., 1907, **91**, 1122; Purvis, *ibid.*, 1909, **95**, 296). In this case the spectrum is similar to that of a simple homologue of pyridine, and the head of the band lies at about 1/λ 3840. This is almost midway between the heads of



I. Full curve: *Piperine.* Dotted curve: *Piperic acid.*
II. *Nicotine.*
III. Full curve: *Cocaine.* Dotted curve: *Benzoic acid.*
IV. Full curve: *Atropine, hyoscyamine and hyoscine.* Dotted curve: *Tropic acid.*

the bands for α- and β-picoline. From the point of view of absorption spectra nicotine may therefore be regarded as a homologue of pyridine.

In cocaine the molecule is much more complex than that of the two alkaloids already considered:



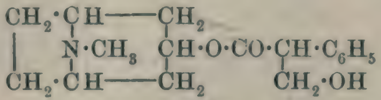
Cocaine.

On boiling with concentrated mineral acids, cocaine breaks up into benzoic acid, methyl alcohol, and ecgonine:

$$\underset{\text{Cocaine.}}{C_{17}H_{21}O_4N} + 2H_2O = CH_3{\cdot}OH + C_6H_5{\cdot}CO_2H + \underset{\text{Ecgonine.}}{C_9H_{15}O_3N}.$$

In this case the unreduced nucleus is a benzoic acid residue, and the spectrum of the alkaloid is identical with that of benzoic acid, as described by Hartley (T., 1907, **91**, 319). The presence or absence of the band in the spectrum of benzoic acid has been the subject of some discussion, but we are able to confirm the existence of the shallow band recorded by Hartley and Hedley (*loc. cit.*).

The case of atropine is of special interest on account of the close connexion of this alkaloid with hyoscyamine and hyoscine:



Atropine.

As is well known, atropine is an optical isomeride of hyoscyamine, and we find that the spectra of these two alkaloids are identical. When atropine is acted on by hydrolytic agents, it splits up into tropeine and tropic acid:

$$\underset{\text{Atropine.}}{C_{17}H_{23}O_3N} + H_2O = \underset{\text{Tropeine.}}{C_8H_{15}ON} + \underset{\text{Tropic acid.}}{C_9H_{10}O_3}.$$

Similar products are given by hyoscyamine. Tropeine is a fully reduced substance, whereas tropic acid contains an unreduced benzene nucleus.

The spectrum of tropic acid is peculiar. It contains two very narrow bands, having their heads at $1/\lambda$ 3770 and $1/\lambda$ 3870; this spectrum is the same as that of atropine and hyoscyamine.

Another point of great interest in connexion with the absorption spectra of this group of alkaloids is that, although hyoscine (*l*-scopolamine), $C_{17}H_{21}O_4N$, differs in composition from hyoscyamine, it gives the same spectrum. The products of hydrolysis of hyoscine are scopoline and tropic acid:

$$\underset{\text{Hyoscine.}}{C_{17}H_{21}O_4N} + H_2O = \underset{\text{Scopoline.}}{C_8H_{13}O_2N} + \underset{\text{Tropic acid.}}{C_9H_{10}O_3}.$$

The constitution of scopoline has not been completely elucidated, but it is known to be a wholly reduced substituted pyridine. The unreduced portion is the same in all three alkaloids, namely, tropic acid; the differences occur entirely in the reduced portion of the molecule, and, as has been pointed out in the case of the cinchonine group of alkaloids (T., 1911, **99**, 1261), such differences may exist without disturbance of the spectrum. The identity of the spectrum of hyoscine with that of atropine and hyoscyamine is thus satisfactorily accounted for.*

In all these cases, therefore, it would appear that the same relation exists as in the earlier cases examined, in which reduced and unreduced rings are conjoined. Whilst absorption appears to be an additive property when the members of the same homologous series are compared with one another, it is remarkable that it is possible to add large groups to such nuclei as quinoline, pyridine, and benzoic acid with only very slight effect on their spectra.

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London.

# CXXIV.—*A Case of Isomerism in the Methylated Ferrocyanides.*

By Ernald George Justinian Hartley.

In a previous communication (T., 1910, **97**, 1729) the author described the preparation of tetramethyl ferrocyanide from hexamethylferrocyanogen chloride, $(CH_3)_6FeC_6N_6Cl_2$, by heating the latter under diminished pressure, two molecular proportions of methyl chloride being given off. An analysis of the crude substance so obtained gave numbers which were in good agreement with the formula $(CH_3)_4FeC_6N_6$, and the percentage of iron in a portion that had been recrystallised from chloroform was practically the same as in the unpurified material. It was concluded therefore that the product was homogeneous except for the presence of a small quantity of impurity due to some slight further decomposition taking place during the heating.

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* Through the kindness of Mr. Francis H. Carr we have been enabled to compare the spectrum of norhyoscyamine with that of atropine, and find that there is no difference between them.

Since that time a considerable amount of the compound has been prepared in this laboratory, and it has been possible to study its properties more fully, with the result that an isomeric substance has been isolated in a pure state. For the preparation on a larger scale the following method was adopted. About 30 grams of the chloride, precipitated by ether from an alcoholic solution and dried over sulphuric acid, were heated to between 140° and 150° in a strong glass retort placed in an air-bath, and exhausted by means of a Fleuss pump. At this temperature gas was freely evolved for about six hours, and in nine hours the evolution had practically ceased. The weight of substance left showed that there was always some decomposition beyond the normal one, and there was invariably a strong odour of *iso*cyanides on opening the apparatus. The contents of the retort were dissolved in about 90 c.c. of hot chloroform, when a pale brown solution was obtained, from which a good crop of crystals, consisting mainly of yellow, rectangular plates, was deposited on cooling. In favourable experiments this crop amounted to nearly 50 per cent. of the substance left in the retort. These crystals contain a large amount of chloroform of crystallisation, which is rapidly given off on exposure to the air, leaving a pale yellow, amorphous powder. This variety will be designated as *α-tetramethyl ferrocyanide.*

On evaporating the chloroform solution, from which the above crop had been removed, on a hot plate, a white, apparently amorphous substance was gradually deposited—almost completely so by the time the liquid had decreased to about half its original bulk. This solid was best separated by filtration on an "alundum" filter. After it is once deposited, it is practically insoluble in chloroform, but can be purified by crystallisation from hot methyl alcohol, from which it separates on cooling, usually in rather short, yellow needles. This substance, which it is proposed to call *β-tetramethyl ferrocyanide*, constitutes about 5 per cent. of the crude material left in the retort. In a large number of preparations it invariably made its appearance at this stage of the process.

On further evaporation of the chloroform, one or two more crops of the α-compound were obtained, each one becoming more contaminated with impurities, consisting partly of unchanged chloride and partly of some dark substance which becomes blue on drying in the air. Finally, a dark, oily residue, from which no further crystals could be obtained, remained, forming a solid blue mass, when all the chloroform had disappeared. On treating this again with warm chloroform, most of the blue matter remained insoluble, and a further small amount of the α-variety could sometimes be extracted.

Since the blue substance was found in much larger quantity when the heating of the chloride had for any reason been excessive, it is concluded that it is not a normal product of the reaction, but is formed by some secondary decomposition. It is soluble in water, forming a pale brown solution, which with ferric chloride gives a strong purple coloration. It was not found possible to isolate any pure substance from this residue.

The various portions of the α-compound were purified by several recrystallisations from chloroform, during which process a very small quantity of the β-variety was occasionally obtained from the later fractions.

An analysis of α-tetramethyl ferrocyanide made on material crystallised three times from chloroform and heated at 97° until constant gave these results:

0·2618 gave 0·4263 $CO_2$ and 0·1056 $H_2O$. C=44·4; H=4·5.
0·4952 „ 0·1451 $Fe_2O_3$. Fe=20·51.

Analyses of the β-form crystallised three times from methyl alcohol, and also heated at 97° until constant, gave:

0·2283 gave 0·3696 $CO_2$ and 0·0920 $H_2O$. C=44·2; H=4·5.
0·2503 „ 0·3970 $CO_2$ „ 0·1018 $H_2O$. C=43·3; H=4·5.
0·2384 „ 0·3830 $CO_2$ „ 0·0965 $H_2O$. C=43·8; H=4·5.
0·7867 „ 0·2299 $Fe_2O_3$. Fe=20·45.

$(CH_3)_4FeC_6N_6$ or $C_{10}H_{12}N_6Fe$ requires C=44·09; H=4·47; Fe=20·55 per cent.

The two substances have therefore the same percentage composition within the limits of analytical errors.

*Properties of the two Isomerides.*—The α-variety is readily soluble in water, methyl alcohol, ethyl alcohol, or chloroform, and insoluble in most of the other usual organic solvents. It separates from concentrated aqueous solutions in very small crystals, which, when dried in the air, contain $2H_2O$. The water is easily given off either by warming or simply keeping over sulphuric acid in a vacuum. As stated above, it separates from chloroform solutions in large, transparent, rectangular plates, which, however, become opaque so rapidly on exposure to air that no attempt was made to determine the amount of combined solvent.

An aqueous solution gives a red colour with ferric chloride; a white, crystalline precipitate with mercuric chloride, which, when examined under the microscope, is seen to consist of rosettes and bundles of short, rather stout needles; and a very fine, yellow, crystalline precipitate with hydrogen platinic chloride. When a fairly concentrated solution is treated with silver nitrate, no immediate precipitate is formed, but after some hours rosettes of white crystals separate. A determination of silver in these agrees with the formula $(CH_3)_4FeC_6N_6,AgNO_3$ (Found, Ag = 24·28. Calc., Ag = 24·39 per cent.). On heating the α-compound with methyl iodide, combination takes place, with the formation of $(CH_3)_6FeC_6N_6I_2$. For example, 1·08 grams were heated for six and a-half hours at 98° with excess of methyl iodide in a sealed tube. The solid matter was then found to weigh 2·07 grams. It was first digested with acetone to remove a small quantity of a periodide (which results from the fact that some free iodine is always liberated from methyl iodide vapour by the heat of sealing the tube), and then warm chloroform was added to dissolve out any unchanged tetramethyl compound.

The residue weighed 1·57 grams. It was soluble in water, methyl alcohol, or hot ethyl alcohol. From the latter solvent, on cooling, it was obtained in pale yellow needles:

0·5602 gave 0·0805 $Fe_2O_3$. Fe = 10·06.
0·3313 „ 0·2795 AgI. I = 45·58.
$C_{12}H_{18}N_6I_2Fe$ requires Fe = 10·07; I = 45·61 per cent.

β-Tetramethyl ferrocyanide is soluble in water or methyl alcohol (though far less so than the isomeride), and practically insoluble in ethyl alcohol, chloroform, or other organic solvents. It can be crystallised readily from hot solutions in either of the two first solvents, separating from water in very fine, long, yellow needles containing $6H_2O$.

In aqueous solution it gives with ferric chloride a red colour similar to that produced by the α-compound.

It forms a white precipitate with mercuric chloride consisting of very fine, hair-like crystals, and a yellow, insoluble platinichloride undistinguishable in appearance from its isomeride.

With silver nitrate even in an extremely dilute solution an immediate white precipitate is formed consisting of such fine crystals that they pass through a filter paper. They are soluble in hot water, but separate at once on cooling. By filtering in an "alundum" filter and washing with alcohol, this double salt can be obtained in a suitable condition for analysis, and is found to contain the same percentage of silver as the corresponding α-compound. (Found, Ag = 24·25. $(CH_3)_4FeC_6N_6,AgNO_3$ requires Ag = 24·39 per cent.) Nitric acid precipitates a rather insoluble crystalline nitrate with the β-, but none even with a concentrated solution of the α-form.

Another important point of difference is observed in its behaviour with methyl iodide.

0·85 Gram of the β-form was heated with excess of methyl iodide in a sealed tube under exactly the same conditions as described above with the α-form. At the end of the experiment the solid matter had only increased in weight to 0·92 gram, and this increase was evidently due to combination with the free iodine* (liberated as mentioned above). No trace of the compound $(CH_3)_6FeC_6N_6I_2$ was found, and nearly the whole of the original substance was recovered unchanged on recrystallising from hot methyl alcohol.

### *Determination of the Molecular Weights.*

For this determination a somewhat novel method was employed, since, owing to the rather insoluble nature of the β-variety, a direct measurement of the osmotic pressure was not possible with the apparatus in use in this laboratory, which is not adapted for pressures less than two atmospheres.

In a paper by Lord Berkeley and the author (*Proc. Roy. Soc.*, 1909, *A*, **82**, 271), it was shown that, when an osmotic cell with the membrane deposited as far as possible on the surface of the porcelain is immersed in a solution, the rate at which water is drawn through the membrane is proportional to the osmotic pressure of that solution, if the latter is not too concentrated. By making use of a slight modification of this method, in which the effect produced by solutions of a number of different substances was compared with that of a compound of known molecular weight (in this case sucrose), it was found possible to obtain results from which this constant could be calculated to within ±3 per cent. of the true value, and within these limits the molecular weight of α- and β-tetramethyl ferrocyanide proved to be identical, and to correspond with the simple formula $(CH_3)_4FeC_6N_6$.

The details and exact figures of these experiments are not given here, as Lord Berkeley and the author hope shortly to make them the subject of a separate communication.

It seems, then, conclusively proved that two isomeric tetramethyl ferrocyanides exist, having quite distinct properties, although there is a similarity in some of their reactions which suggests that the structural difference is not very great. There is a possibility that the uncrystallisable residue contains one or more further isomerides in small quantity, although so far it has not been found possible to isolate any other pure compounds.

It should be noted here that no indication of isomerism was observed when dealing with the hexamethyl ferrocyanogen salts, several of which were prepared and crystallised in fairly large quantities previous to this work. It must therefore be assumed that the separation into two forms takes place during the heating of the hexamethylferrocyanogen chloride, since if it were brought about during the subsequent treatment, namely, solution in chloroform, there should be a further deposition of the β-variety to about the same extent on each recrystallisation of the α-form from that solvent, whereas only very small quantities were ever obtained during this operation, and none at all after the α-compound had been purified. At present no means have been found to convert one form into the other.

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* All the various methylated ferrocyanogen compounds so far described appear to form periodides with free iodine.

The cases of isomerism hitherto observed in this family of compounds are the α- and β-ferricyanides discovered by Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413), and the α- and β-ferrocyanides described more recently by Briggs (T., 1911, **99**, 1019). Lately, however, some doubt has been thrown on the existence of the former by Hauser and Biesalski (*Ber.*, 1912, **45**, 3516).

Whether the isomerism of the methylated and metallic ferrocyanides respectively is due to the same cause it is impossible to state, but the differences in chemical and physical properties seem on the whole to be considerably greater in the case of the former, with the exception of the marked difference of colour observed by Briggs in the salts, and not found by the author in the alkyl derivatives. With regard to the nature of the isomerism, Briggs (*loc. cit.*) proposed a modified form of Werner's "co-ordination" system, whilst the author has pointed out (T., 1911, **99**, 1553) that, if one of the ordinary structural formulæ, such as Browning's, is adopted, there is the possibility of isomerism due to carbon linked to nitrogen by double bonds, such as occurs in the oximes, etc. However, until more experimental evidence is forthcoming, it appears premature to discuss this point at any length.

With the object of throwing more light on the constitution of the double cyanides, the author is at present investigating the alkyl cobalticyanides, and has obtained fairly conclusive evidence that these compounds afford another example of isomerism, but the work is not quite complete.

These experiments have been carried out in Lord Berkeley's laboratory at Foxcombe, to whom the author's best thanks are due.

# CXXV.—*Solubilities of Salts of Ammonium Bases in Water and in Chloroform. Part I. Solubility as a Constitutive Property.*

By CYRIL JAMES PEDDLE and WILLIAM ERNEST STEPHEN TURNER.

THE measurements recorded in this paper were prompted partly by observations we had previously made in connexion with the relation of the solubility of substances to their state of molecular aggregation (Peddle and Turner, T., 1911, **99**, 685; Turner, *ibid.*, 1911, **99**, 880).

It was pointed out in the second of the two communications referred to that miscibility of two substances was possible when both were normal or both associated, but that solubility was limited when one substance was normal and the other associated; and in support of the rule various illustrations were given, both in connexion with the miscibility of liquids and the solubility of solids in liquids.

In addition to the evidence there quoted, certain other generalisations connecting the properties of molecular weight, solubility, and dielectric constant can be shown to lead to the view that the solubility of a substance should be connected with its degree of association. The first of these generalisations is that of Walden (*Zeitsch. physikal. Chem.*, 1906, **55**, 683) to the effect that the solubility of salts—similar in type to those we have employed—is greater the more highly associated the solvent.

Two other generalisations, taken in conjunction, must also lead at once to the same view. Of these two, the first is also due to Walden (*Zeitsch. physikal. Chem.*, 1908, **61**, 633), and states that the solubility of a normal electrolyte (for example, tetraethylammonium iodide) is greater the higher the dielectric constant of the solvent. This result was established after the examination of thirteen organic liquids, and a quantitative relationship of an empirical character obtained, namely, that the ratio $\epsilon / \sqrt[3]{\mu}$, where $\epsilon$ is the dielectric constant of the liquid and $\mu$, the molecular solubility of the electrolyte, is a constant quantity.

The second of the two generalisations is the well-known Nernst-Thomson rule, which may be stated in the form that the molecular weight of a substance capable of association or dissociation is greater the smaller the dielectric constant (see Turner, *loc. cit.*).

Hence, we expected to find a general connexion between the degree of association of a salt and its solubility in a given solvent.

We may say at once, however, that we have not, under the conditions of experiment described below, been able clearly to establish the connexion we sought.

The data we have adduced, however, furnish information for the solution of several other interesting problems. In the first place, the character of the salts used, derived in many cases either from isomeric bases or from homologues, makes it possible to ascertain whether any additive relationships can be discovered in connexion with solubility, or whether the property is a constitutive one.

Moreover, the discovery of a non-ionising substance, like chloroform, as a solvent for salts is, in itself, important, in that it allows a comparison to be made of the properties of salt solutions in two media of quite opposite character. Walden's work consisted in the examination of but few salts in a large number of liquids. The present investigation, on the other hand, deals with many salts, derived from the substituted ammonium bases and also triethylsulphonium iodide, and only two solvents, water and chloroform. We purpose making a comparison of several properties of solutions in these solvents, contrasting in this first paper the solubility data at a temperature of 25°; whilst in a second communication we hope to give the results of an investigation on the effect of the addition of a second salt on these solubilities.

## EXPERIMENTAL.

The twenty-four substances used in the investigation include all types of substituted ammonium salts—chlorides, bromides, and iodides—salts of which the molecular weights in chloroform solution have been recorded in a former paper (Turner, *loc. cit.*).

The method of carrying out the solubility determination differed somewhat according as the solvent was water or chloroform. In both cases samples of the salts were thoroughly dried and finely powdered and analysed repeatedly as a check on their purity and freedom from moisture. When water was the solvent, excess of the salt was stirred in a Jena test-tube with water redistilled from acidulated permanganate, until a constant concentration was attained, the temperature variation of the thermostat used being less than 0·1°. The time required to reach constant concentration varied with the salt, but, with one or two exceptions, no measurement was accepted until the solution had been at least twenty-four hours in the bath, and stirred for at least five. As a rule, the time was much longer. A quantity of the solution varying between 2 and 5 grams was then removed to a weighing bottle by means of a pipette, previously warmed to 60—80°, and provided with a plug of cotton-wool at the tip, and the precise weight of solution determined. After dilution to a known volume, the solution was analysed by Volhard's method by titration with silver nitrate and thiocyanate.

The chloroform used was purified by allowing it to remain for many hours over concentrated sulphuric acid, washing repeatedly with water, drying over calcium chloride, and fractionating to two- or three-hundredths of a degree. Small, brown, stoppered bottles were used for the solubility determinations in chloroform in order to diminish the tendency to decomposition which the bromides and particularly the iodides show when exposed, in this solvent, to the light. The mixture of salt and solvent was warmed to about 40° and then allowed to remain for many hours (twenty-four to one hundred and ten) at 25°, with frequent agitation. The solution, removed and weighed as with aqueous solutions, was placed in a vacuum desiccator, the chloroform slowly removed, and the residue dissolved in water and titrated. With several chlorides, such as propylamine, *iso*butylamine, and *iso*amylamine hydrochlorides, which could be heated to 110° without any decomposition, determinations of solubility were also made by evaporation.

The substances are tabulated in series, and the solubility results are expressed under $P$ as grams of salt dissolved by 100 grams of solvent, under $100n/N$ as molecular percentage solubility, $n$ representing molecules of solute, $N$ of solvent.

In order to avoid repetition at a later stage, we have also inserted in the table the relative degrees of association of the various salts in chloroform solution at the common concentration of 25 milligram molecules per 100 grams of solvent. These factors, denoted by $A$, have been drawn from the measurements of one of us (Turner, T., 1911, **99**, 880).

The following notes should be made on certain of the solutions:

*Aqueous Solutions.*—Several were slightly coloured through keeping for a prolonged time, the following solutions being slightly yellow or brown: ethylamine and diethylamine hydrochlorides; diethylamine hydrobromide and tetraethylammonium bromide; diethylamine hydriodide; propylamine and dipropylamine hydrochlorides; triethylsulphonium iodide. Solutions of ethylamine hydrochloride and tetraethylammonium chloride were very viscous.

*Tetraethylammonium Iodide.*—Walden (*loc. cit.*) quotes two solubility values, namely, 32·9 and 31·44 grams per 100 grams of solution. Calculated on the same basis, our value is 31·0 grams, corresponding with the lower figure. Since these results, which agree, his and our own, were obtained by employing different processes, the lower number is probably correct.

*Solubilities at 25° in Water and in Chloroform.*

| Substance. | M.W. | In water. | | In chloroform. | | |
|---|---|---|---|---|---|---|
| | | *P.* | 100*n*/*N*. | *P.* | 100*n*/*N*. | *A.* |
| $NH_4Cl$ | 53·5 | *39·3 | 13·24 | 0·0 | 0·0 | — |
| $NH_2Et,HCl$ | 81·5 | 279·9 | 61·83 | 0·17 | 0·25 | — |
| $NH_2Pr^a,HCl$ | 95·5 | 278·2 | 52·45 | 5·26 | 6·56 | (8) |
| *iso*$C_4H_9{\cdot}NH_2,HCl$ | 109·5 | 238·9 | 37·48 | 11·56 | 12·63 | 4·63 |
| *iso*$C_5H_{11}{\cdot}NH_2,HCl$ | 123·6 | 192·2 | 28·16 | 5·10 | 4·92 | 5·92 |
| $NHMe_2,HCl$ | 81·5 | 369·2 | 81·57 | 16·91 | 24·77 | 3·92 |
| $NHEt_2,HCl$ | 109·5 | — | 38·06 | — | — | — |
| $NHPr_2,HCl$ | 37·6 | 165·3 | 21·63 | 47·24 | 40·98 | 2·11 |
| $NH_2Et,HCl$ | 81·5 | — | 61·83 | — | — | — |
| $NHEt_2HCl$ | 109·5 | 231·7 | 38·06 | 29·45 | 32·09 | 2·63 |
| $NEt_3,HCl$ | 137·6 | 137·0 | 17·94 | 17·37 | 15·07 | 1·62 |
| $NEt_4,Cl$ | 165·6 | 141·0 | 15·35 | 8·24 | 5·93 | 5·12 |
| $NH_4Br$ | 97·96 | *77·0 | 14·16 | 0·0 | 0·0 | — |
| $NHEt_2,HBr$ | 154·0 | 311·6 | 36·64 | 46·65 | 36·11 | — |
| $NEt_3,HBr$ | 182·1 | 150·6 | 14·91 | 23·44 | 15·37 | 1·78 |
| $NEt_4Br$ | 210·1 | 279·5 | 23·96 | 25·01 | 14·21 | 7·2 |
| $NHEt_2,HI$ | 201·0 | 377·2 | 33·79 | 71·56 | 42·50 | — |
| $NEt_3,HI$ | 229·0 | 370·0 | 29·09 | 92·2 | 48·05 | 2·52 |
| $NEt_4I$ | 257·0 | 45·0 | 3·15 | 1·55 | 0·72 | — |
| $NPr^a{}_4I$ | 313·1 | 18·64 | 1·07 | 54·56 | 20·81 | 4·40 |
| $N(C_5H_{11})_4I$ | 425·3 | 0·74 | 0·03 | 210·8 | 59·17 | 2·17 |
| $NH_2Ph,HCl$ | 129·5 | 107·1 | 14·88 | — | — | — |
| $NHPhMe,HCl$ | 143·5 | 378·8 | 47·54 | — | — | — |
| $CH_2Ph{\cdot}NH_2,HCl$ | 143·5 | 50·6 | 6·35 | 0·0 | 0·0 | — |
| $NH(CH_2Ph)_2,HCl$ | 233·6 | 2·17 | 0·17 | 0·37 | 0·19 | — |
| $N(CH_2Ph)_3,HCl$ | 323·6 | 0·61 | 0·03 | 11·41 | 4·21 | 1·26 |
| $SEt_3I$ | 246·1 | 431·0 | 31·56 | 47·7 | 23·14 | 7·6 |
| $C_9H_7{\cdot}NEtI$ | 285·0 | 301·3 | 18·99 | 1·78 | 0·75 | — |

* These values have been obtained from the tables in Seidell's "Solubilities of Inorganic and Organic Substances."

*Tetraisoamylammonium Iodide.*—Solution difficult to titrate unless very dilute.

*Quinoline Ethiodide.*—Solution dark red and oily. On addition of water, solution became viscid at first, and a yellow deposit appeared to be formed, but further addition of water gave a clear solution with only a slight yellow tinge.

*Chloroform Solutions.*—Several substances gave yellow or brown solutions, but when evaporated the chloride and bromide residues were usually quite white. Tetraethylammonium iodide, quinoline ethiodide, and tetrapropylammonium iodide solutions were deep red.

*Tetraisoamylammonium Iodide.*—Solution light yellow and viscous as glycerol. Solubility determined only by evaporation in a vacuum desiccator (ten weeks required for constancy of weight).

*Benzylamine Hydrochloride.*—No weighable deposit from 7 grams of solution.

*Tribenzylamine Hydrochloride.*—Solubility determined by evaporation, heating to 110°, and placing under diminished pressure.

*Triethylsulphonium Iodide.*—This substance undergoes decomposition in chloroform. A solution of the salt, 0·6074 gram in 5 c.c. of chloroform, was allowed to remain for forty-three hours in the bath, and was then evaporated under diminished pressure, and the residue determined by titration. A loss of 22·2 per cent. of the salt was found to have occurred. Two other solutions, a dilute and a concentrated, were then prepared, and allowed to remain at 25° for half an hour only, after which they were evaporated at the ordinary temperature and under diminished pressure. The first solution contained 0·5040 gram of salt in 6·3568 grams of solution (7·7 per cent.), the second 1·9976 grams in 5·1378 (39 per cent.). The residues determined by titration were 0·5044 gram and 1·990 grams respectively.* Evidently no appreciable decomposition occurred during the process of evaporation, and the dry salt itself has also been found to be quite stable under diminished pressure at the ordinary temperature. Probably, therefore, the figure quoted in the table does, or very nearly does, represent the actual solubility of triethylsulphonium iodide in chloroform.

### *Discussion of Results.*

### *Solubility in Water.*

Great variation is exhibited in the solubilities of the salts, the mono- and di-substituted ammonium chlorides and triethylsulphonium iodide, for example, standing out in marked contrast with di- and tri-benzyl ammonium chlorides or tetra*iso*amylammonium iodide.

The more important points are summarised as follows:

(1) Substitution of a hydrogen atom in an ammonium salt by an alkyl group very greatly increases the solubility (compare ammonium chloride, ethylamine hydrochloride, propylamine hydrochloride, etc.). Aromatic groups, such as the phenyl or benzyl group, are either much less effective in increasing the solubility or even decrease it. The difference between the aliphatic and aromatic radicles is strikingly brought out by a comparison of aniline with methylaniline hydrochloride, the solubility of the latter being more than three times that of the former.

(2) When similarly constituted salts are compared, solubility in water decreases as the mass increases.

It is only by confining the comparison most strictly to similar substances that such regularity can be observed. The great difference between the effects of aliphatic and aromatic radicles already discussed at once marks solubility as a highly constitutive property.

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* We are indebted to M. C. C. Bissett for making these experiments.

An attempt has been made to test whether any additive relations exist, since the substances examined are so related as make this comparison possible.

Among the chlorides are four pairs of isomeric substances, namely, the hydrochlorides of ethylamine and dimethylamine; of diethylamine and *iso*butylamine; of triethylamine and dipropylamine; and of methylaniline and benzylamine. Only in one case, the second mentioned, is there agreement between the values of molecular solubility, and in one case there is very wide divergence. Lack of agreement between isomerides, however, does not necessarily mean the absence of any additive relationships, as is well known. Comparing the homologues in the first three series in the table of solubilities, neglecting ammonium chloride, and making no comparison between *n*-propylamine and *iso*butylamine hydrochlorides, we have as differences between the members compared, in the first series 9·38 and 9·32; in the second, between salts of secondary amines, 2 × 21·75 and 2 × 8·2; in the third, 2 × 11·3, 2 × 10·1, and 2 × 1·3. These differences in the molecular solubility, set out in terms of a difference of composition of $CH_2$, do not raise any great hope of discovering additive relationships, although the persistent recurrence of an average difference value of about 9 units may not be without significance.

Whatever the outcome of further and more exhaustive investigation of substances of precisely similar constitution, it is obvious that the solubility of salts in water must be written down as almost wholly, if not wholly, a constitutive property.

(3) The constitutive character of solubility is also borne out in the effect exercised by the negative radicle, and it is not possible to say definitely whether the chloride, bromide, or iodide will have the greatest solubility in water.

### *Solubility in Chloroform.*

Compared in the usual sense (values of $P$), the salts appear to be distinctly less soluble in chloroform, on the whole, than in water. The surprising thing is that they are so soluble. In most other organic solvents of low dielectric constant, such as ether, benzene, carbon disulphide, carbon tetrachloride, and ethylene dibromide, their solubilities are exceedingly small, and from experiments we have carried out they are much more soluble in chloroform than in acetone. The magnitude of the solubility is all the more striking when reduced to terms of molecular solubility, when the numbers, taken as a set, are but little less than in water as solvent. Solubility in chloroform is therefore exceptional. It does not appear to depend on the fact that all the salts used in this investigation are haloids, for, from the experience of one of us, nitrates are likewise very soluble, and so also are various other salts containing still other negative radicles. There is no doubt that in this respect chloroform is a somewhat exceptional although at the same time a valuable solvent. Compared with water, it is often to be found that the greater the solubility in water the smaller it is in chloroform, and vice versa; but there are quite a number of exceptions. It is obvious that in comparing a series of salts, a point will be reached at which solubility in water and in chloroform will be nearly the same. This applies in all probability to the triethylamine salts, possibly also to those of diethylamine, the solubilities of which in chloroform appear exceptionally high. Other points to which attention may be called briefly are:

(1) As in water, so also in chloroform, the solubility of an ammonium salt is greatly increased by the introduction of organic radicles, the aliphatic again having a much greater effect than the aromatic. Although we have made no exact measurements with aniline and methylaniline hydrochlorides, we have found that the former may be regarded as insoluble, whilst the latter is very soluble in chloroform.

(2) As a rule, increase in molecular weight is accompanied by increase of solubility. This rule is only strictly preserved when series of similarly constituted salts are compared (compare, for example, the monoalkylamine and dialkylamine salts as two series, as also the tetraethyl-, propyl-, and *iso*amyl-ammonium iodides). *iso*Amylamine hydrochloride is an exception even under these conditions.

(3) No suggestion of additive relationships occurs either by a comparison of isomerides or of homologous substances.

(4) With the exception of tetraethylammonium iodide, the order of increasing solubility is chloride, bromide, iodide, so far as investigated.

The absence of any definite connexion between solubility in water and in chloroform and chemical composition of the above salts may well give rise to the question as to whether any physical property of either component of the solution may affect the extent to which miscibility may occur, and this leads back to one of the objects of the investigation, namely, the effect of molecular association on solubility.

It is very possible that this factor has an influence. In the solid state these salts must be regarded as built up of complex molecules; in aqueous solution they appear dissociated, in chloroform strongly associated. Now in accordance with the rule mentioned in the introduction, that two substances which are both associated will readily mix, it should be found that the strongly associated salts should be the ones most soluble in water. A strict test of the rule requires a knowledge of the molecular state of the salt in saturated solution, and this is not known except in a few cases. The association factors for dilute solution do largely indicate the relative order of complexity for much stronger solutions, however, and, recognising this, the table on p. 1205 shows that the rule holds, generally speaking, although the order of association is in many cases not that of solubility. As to solubility in chloroform, it can be pointed out that when similarly constituted salts, such as the monosubstituted amine salts, the disubstituted salts, and the tetraalkylammonium iodides are compared in series, then the solubility increases as the degree of association decreases. Some doubt may be felt as to the sufficiency of this illustration, and in view of the fact that the iodides, the most associated salts, are in several cases nevertheless the most soluble, it must be admitted that molecular association cannot be the deciding factor in solubility. That it is a factor is probable from what has been said already, and in the series of monoalkylamine hydrochlorides, *iso*amylamine hydrochloride is abnormal in being more associated than *iso*butylamine hydrochloride, and, in conjunction with this, also has the smaller solubility, which is also abnormal. If it be admitted that molecular association is a factor affecting solubility, it is not unlikely that if a solvent like ethyl alcohol be employed, which, one of us has found, neither permits either marked association nor ionisation, greater regularity might be found to exist among the solubilities observed.

We hope further to discuss this point in a later communication, and to examine in some detail the relationship between solubility and dielectric constant and between dielectric constant and molecular weight, which, as already indicated in the introduction, suggest the connexion between molecular state and solubility.

We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed much of the expense entailed by this investigation.

THE GRAMMAR SCHOOL,
BARNSLEY.

THE UNIVERSITY,
SHEFFIELD.

# CXXVI.—*The Mode of Combustion of Carbon: the Effect of Drying the Oxygen.*

By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

ARMSTRONG and Colgate, in a recent paper (*J. Soc. Chem. Ind.*, 1913, **32**, 391), have suggested that water (as an electrolyte) plays an all-important part in determining the manner in which carbon burns.

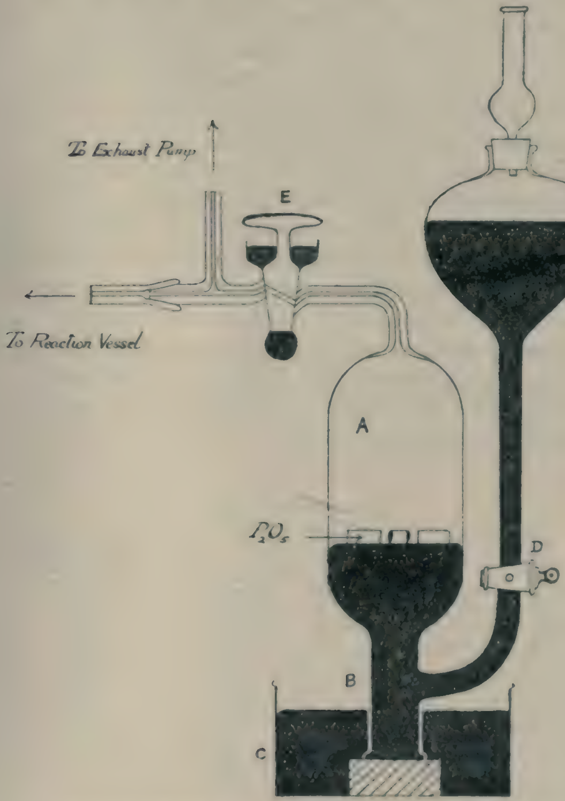
The experiments recorded in our paper, "The mode of combustion of carbon" (this vol., p. 461), wherein we advanced a hypothesis that the first reaction between oxygen and carbon results in the formation of a loosely combined "physico-chemical complex," were made with air or oxygen dried by contact for several days with concentrated sulphuric acid. We also made a number of experiments with air dried by contact with phosphoric oxide, the results of which were not recorded in that paper, but of which a record seems desirable.

H. B. Baker, in his work on combustion in dried oxygen, referred to in our previous papers, used purified sugar charcoal, which, from the details of the experiments given, appears to have been "saturated" with oxygen at a low temperature before being raised to the experimental temperature.

The most striking result of his experiments, apart from the difficulty with which the dried oxygen combined with the carbon, was the large proportion of carbon monoxide found in the products of combustion. Thus, when oxygen which had been dried by contact with phosphoric oxide during three weeks was passed over carbon contained in a hard glass tube and heated to bright redness with a gas blowpipe, no visible combustion occurred, and the gases that passed over had the following percentage composition:

| | |
|---|---|
| Carbon dioxide | 2·2 |
| Carbon monoxide | 39·5 |
| Oxygen | 58·1 |

It being well known that dried oxygen and carbon monoxide unite with great difficulty, Baker naturally contended that since this method of rendering the conditions unfavourable to the oxidation of carbon monoxide resulted in the production of an increased quantity of that gas when carbon was burnt, one is justified in regarding it as, in all probability, the first product of combustion. By this, we believe, he intended to convey the suggestion that carbon monoxide is the "first product" so far as carbon dioxide is concerned—that it does not arise from reduction of carbon dioxide; but that all, or most, of the carbon dioxide found in the products of combustion of carbon by "moist" oxygen at a bright red heat arises from the subsequent oxidation of carbon monoxide; for his results in no way preclude the possibility of the preliminary formation of a complex or compound other than carbon monoxide or carbon dioxide. On the contrary, if our hypothesis regarding the mode of combustion of carbon is correct, Baker's experiments should afford information regarding the ratio in which carbon dioxide and carbon monoxide appear as the decomposition products of the "complex" at different temperatures; for the extreme dryness of the oxygen would prevent its reaction with carbon monoxide, and would thus "fix" or "freeze" the ratio.



It is necessary, however, to consider whether dryness of the oxygen affects in any way the formation of the "complex." To determine this we have made pairs of experiments with dried and undried air in the following manner.

The quartz bulb employed for the fixation experiments described in our previous paper (*loc. cit.*, p. 473) was used as the reaction vessel, and a gasholder for drying the air over phosphoric oxide was attached by a ground joint. This gasholder had the form shown in the diagram. The gas reservoir *A* was filled with freshly boiled and distilled mercury, the wide tube *B* being open and standing over mercury in the trough *C*, and the tap *D* leading to the mercury reservoir being closed. Dry air was then passed up under the mercury in the trough until the reservoir was about three parts full, and eight or nine plugs of freshly purified phosphoric oxide were introduced. The wide entrance tube was then closed under the mercury in the trough by a rubber pad, and the apparatus left for several weeks.

Before making the experiment the reaction tube was heated to 1100°, and exhausted during forty-eight hours at that temperature. The temperature was then lowered to the experimental temperature, and the dried air introduced to the vacuous reaction vessel by quickly opening the mercury-cup tap *E*, the tap *D* leading to the reservoir of dry mercury being opened.

Heating was continued during a given length of time, and the residual gases then pumped out.* The temperature of the carbon was then raised to 1100°, and the gases evolved were collected.

The following are typical results:

*Temperature* 200°.

| Duration of heating. | Undried air, 10 mins. | Air dried during 4 weeks over phosphoric oxide. | |
|---|---|---|---|
| | | 10 mins. | 5 mins. |
| Residual gas: † volume c.c. | 22·79 | 24·87 | 25·13 |
| Analysis $CO_2$ | 2·45 | 2·30 | 2·15 |
| $O_2$ | nil | nil | nil |
| CO | nil | nil | nil |
| Gas evolved at 1100°: ‡ volume c.c. | 9·47 | 9·73 | 10·05 |
| Analysis $CO_2$ | 10·55 | 12·65 | 12·20 |
| $O_2$ | nil | nil | nil |
| CO | 89·10 | 86·85 | 87·35 |
| Oxygen burned, c.c. | 5·87 | 6·05 | 6·17 |
| Percentage of oxygen burned appearing as: | | | |
| $CO_2$ | 9·6 | 9·4 | 8·8 |
| CO | nil | nil | nil |
| "$C_xO_y$" | 90·4 | 90·6 | 91·2 |

A temperature as low as 200° was chosen because we wanted, if possible, unburned oxygen to remain at the end of the experiments, whether the air was dried or undried. For the same reason the duration of heating was made as short as the experimental method would allow.

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* A phosphoric oxide drying tube was fused between the Sprengel mercury pump and the reaction vessel.

† Termed "final gas" in our previous paper.

‡ Termed "$C_xO_y$ gas" in our previous paper.

It will be seen that there is practically no difference between the results of the experiments with dried air and that with undried. No measurable quantity of carbon monoxide was present in the gases that remained over the carbon at 200°, nor was there any unburned oxygen.

We conclude from these experiments that the formation of the "complex" is in no way prevented by the drying of the oxygen. It would appear therefore that its decomposition is accelerated by the presence of moisture, for Baker has clearly shown that moisture (to the extent that would be present in air dried by concentrated sulphuric acid) accelerates the "combustion" of carbon—accelerates the formation of carbon monoxide and carbon dioxide. If, as we assume, these two gases arise from the decomposition of a complex first formed, and there is no retardation in the formation of the complex by drying, it must follow that its decomposition is prevented or minimised by the absence of moisture.

In this connexion it may be recalled that C. J. Baker (T., 1887. **51**, 249) found that after well-dried oxygen had been admitted to purified carbon at a low temperature ($-12°$), only traces of gas (carbon dioxide) were evolved on heating to 150°, or by stages of 50° up to 350°. On raising the temperature to 450°, however, a slow but regular evolution of gas (mainly carbon monoxide) took place.

Circumstances prevent us at present from pursuing further the question of the influence of moisture, or it would have been of interest to have repeated the series of "fixation" experiments recorded in our previous paper, using air dried by phosphoric oxide. For, as already suggested, by preventing or retarding the combustion of carbon monoxide by this means, a nearer approach to the true ratio in which carbon dioxide and carbon monoxide arise from decomposition of the complex would be obtained than by relying, as we did in our experiments with "undried" air, on the rapid removal of the oxygen from the sphere of action by "fixation."

One experiment with air dried over phosphoric oxide during sixteen days, and admitted to purified carbon at 300°, can be compared with the corresponding experiment with "undried" air given in our previous paper.

*Dried Air at* 300°.

| Duration of heating. | 30 minutes. |
|---|---|
| "Final gas": volume c.c. | 19·87 |
| Analysis $CO_2$ | 4·10 |
| $O_2$ | nil |
| CO | 0·50 |
| "$C_xO_y$ gas": volume c.c. | 6·84 |
| Analysis $CO_2$ | 11·20 |
| $O_2$ | nil |
| CO | 88·40 |
| Oxygen burned, c.c. | 4·65 |
| Percentage of oxygen burned appearing as: | |
| $CO_2$ | 17·6 |
| CO | 1·1 |
| $C_xO_y$ | 81·3 |

This result differs in no important respect from that of the corresponding experiment with undried air (*loc. cit.*, p. 476). The ratio $CO_2/CO$ in the "final gas" is 8·20 in the "dried," as compared with 8·60 in the "undried" experiment.

ESKMEALS.

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## CXXVII.—*Studies of Dynamic Isomerism. Part XV. The Influence of Light on Isomeric Change.*

By THOMAS MARTIN LOWRY and HAROLD REUBEN COURTMAN.

THE isomeric changes which have been studied in previous papers of this series have been shown to be exceedingly sensitive to the influence of various chemical agents. A climax was probably reached when it was found that the stimulating influence of piperidine on solutions of nitrocamphor in benzene could still be detected at a dilution of 1 part in 100 millions, or 1 centigram per 1000 kilos. Carbonyl chloride, on the other hand, as a natural impurity in chloroform or an added impurity in other solvents, was capable of arresting this isomeric change by eliminating basic impurities in the form of inactive carbamides; in the presence of this "anti-catalyst" an absolute arrest of isomeric change was maintained, in one instance at least, during a period of nearly a month.

Under these conditions it was a matter of great interest to find out how these very sensitive changes would be influenced by exposing the solutions to a powerful light.

Such experiments were the more important in view of the remarkable influence exerted by light upon the relatively sluggish change of maleic into fumaric acid in presence of bromine (Bruner, *Bull. Acad. Sci. Cracow*, 1910, 192), and of *allo*cinnamylideneacetic acid, $C_6H_5\cdot CH{:}CH\cdot CH_2\cdot CO_2H$, into its more stable stereoisomeride in the presence of iodine (Liebermann, *Ber.*, 1895, **28**, 1438, 1443). These changes do not usually take place at all except in the presence of a large quantity of an added catalyst, such as concentrated hydrobromic acid; the readiness with which they take place on exposure to light indicates that this may provide a very powerful weapon for promoting change. This conclusion is supported by the fact that the internal oxidation-reduction of nitrobenzaldehyde to nitrosobenzoic acid,

$$NO_2\cdot C_6H_4\cdot CHO \longrightarrow NO\cdot C_6H_4\cdot CO_2H,$$

is readily effected by exposure to light, even when the substance is in the solid state.

About ten years ago, when silica glass was first introduced, attempts were made to study the influence of ultra-violet light on some of the more facile isomeric changes, by exposing a solution in a silica polarimeter tube to the light of an arc. It was soon realised, however, that trustworthy conclusions could only be drawn if the solution was maintained at constant temperature. The rapid progress which has been made in the production of silica apparatus, together with the development of the silica-mercury lamp, has now made it easy to carry out critical experiments by methods that would have been impossible a few years ago. The observations now described were carried out with the help of a silica-jacketed, silica polarimeter tube (*Trans. Faraday Soc.*, 1913, **8**), through the outer jacket of which distilled water, at a constant temperature of 20°, was circulated. The solution in the inner tube, protected in this way from purely thermal influences, was exposed to dazzling radiation from a silica mercury lamp (*Trans. Faraday Soc.*, 1912, **7**, 269, Fig. 2), running parallel to the central tube and at a distance of about 5 cm. from it. The radiation, which was much more powerful than sunlight, and contained a wide range of brilliant ultra-violet rays, was generally allowed to act on the solutions for an hour at a time. During this period no polarimetric readings could be taken, but by tracing the course of the mutarotation curve before and after exposure to light, it was easy to see whether isomeric change had been stimulated in any degree by this powerful "insolation."

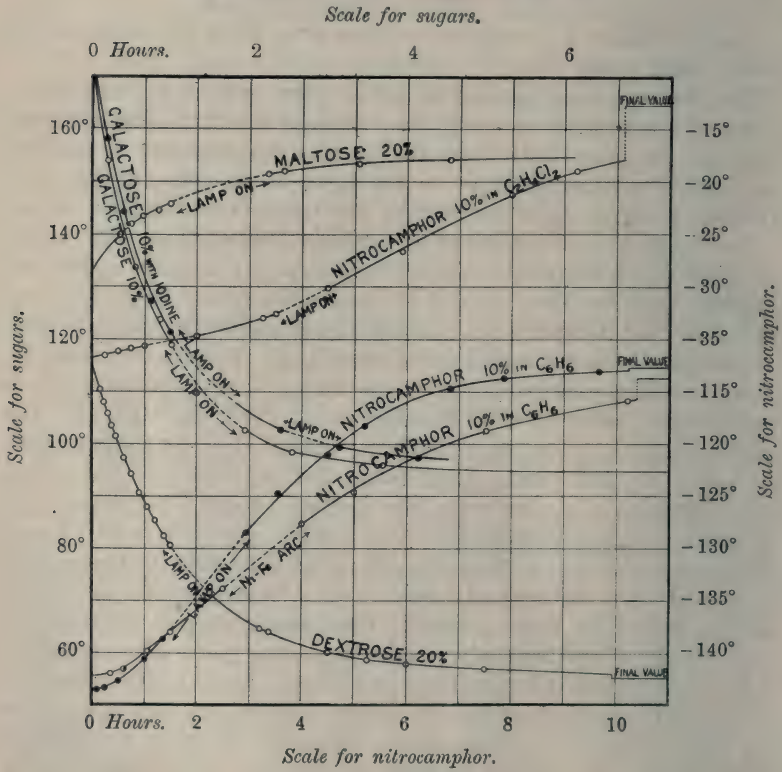
*The Sugars.*—The three sugars selected for examination were dextrose, galactose, and maltose. The two former were highly purified specimens which had been soaked in a mixture of alcohol and water during eight years in order to convert them wholly into the least soluble form. The maltose was a commercial specimen.

Each sugar was examined in an aqueous solution; the galactose was also examined in an aqueous solution, to which iodine had been added. The four curves reproduced in Fig. 1 indicate the limits of the change of rotatory power when mercury green light of wave-length 5461 is substituted for sodium light. The four curves agree in showing not the slightest acceleration by exposure to the light of the mercury arc.

*Nitrocamphor.*—This substance was examined both in ethylene chloride (which had not been used previously for this purpose) and in benzene, these solvents being selected as typical diactinic and absorbent media. The solution in benzene was exposed to the light of an iron-nickel arc, which gives a very crowded line-spectrum, as well as to the light of the mercury arc, which gives a more open spectrum containing a smaller number of very powerful lines. The

Fig. 1.

*Mutarotation of nitrocamphor and the sugars.*

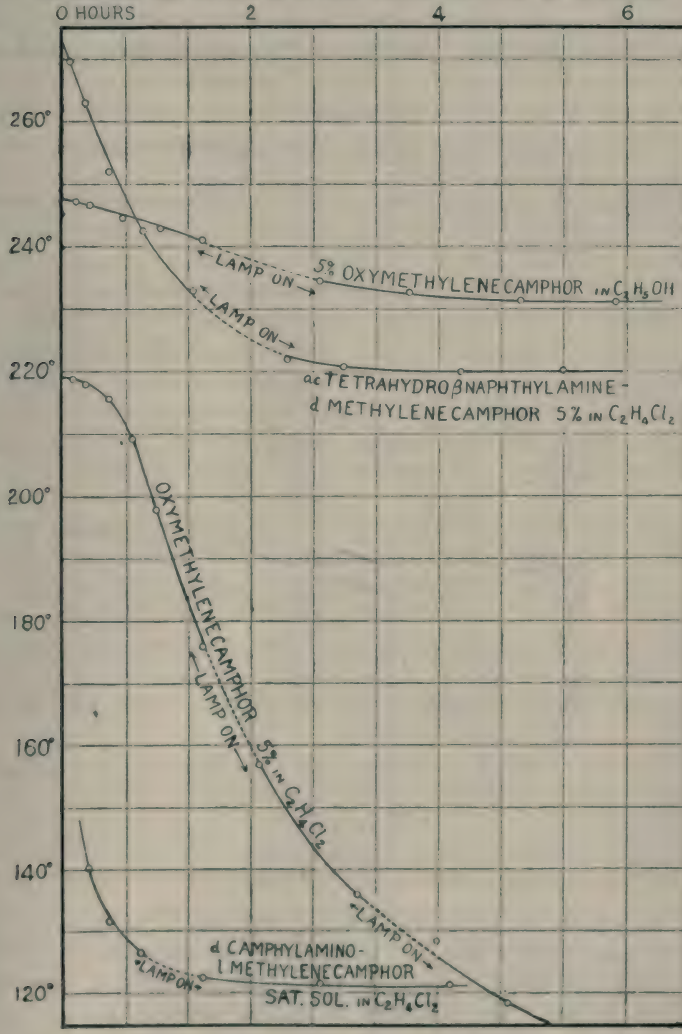


three curves shown in Fig. 1 again show no acceleration whatever.

*Hydroxymethylenecamphor.*—This substance could only be used

FIG. 2.

*Mutarotation curves for hydroxymethylenecamphor and its derivatives.*

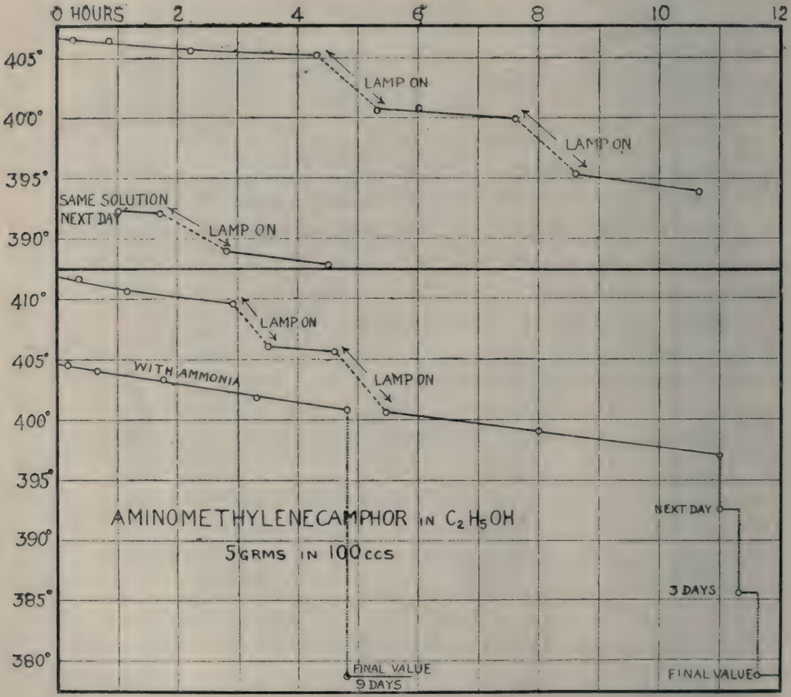


after it had been distilled in a current of steam in order to remove acid impurities, thus reducing the velocity of isomeric change to within reasonable limits. It was examined in alcohol, where the change of rotation is very small, and in ethylene chloride, where the range is very large. Negative results were again obtained, as also in the case of two amino-derivatives prepared by Prof. Pope, for which curves are given in Fig. 2.

*Aminomethylenecamphor.*—These negative results are the more remarkable in view of the striking effects produced in the case of the closely related aminomethylenecamphor by exposure to light under precisely similar conditions. The curves shown in Fig. 3 need very little explanation. The normal rate of change was slow, so that even after a day had elapsed the change was still far from complete; the addition of ammonia exerted only a very slight catalytic action. On exposure to light, however, the substance immediately responded by changing with great rapidity. On removing the stimulus, the change reverted to its original slow rate, but could be accelerated again by a further exposure to light. A rapid change could be induced in this way even when the slower

FIG. 3.

*Influence of light on the mutarotation of aminomethylenecamphor.*



change had been proceeding during a whole day. The vertical dotted lines in the lower part of the figure are not mutarotation curves, but are used merely to link together observations made on different days.

*a-Benzoylcamphor*.—Special interest attaches to this substance, in reference to the "enolic" form of which Forster (T., 1901, **79**, 1001). writes that "On exposing a freshly prepared solution to sunlight, the rapidity of the change becomes greatly exaggerated, the position of equilibrium being reached in two or three hours," instead of in six days. Attention was directed at the same time to the stability of the colourless crystals of the enolic isomeride, "a solution in chloroform having been preserved in darkness during twelve hours, exposed to bright sunlight during two hours, and even sown with a crystal of the ketonic isomeride, without suffering any perceptible reduction in optical activity." It is very probable that, as in the case of nitrocamphor, carbonyl chloride was here acting as an "anti-catalyst," and producing an arrest of isomeric change.

Attempts to study the action of light on this substance when dissolved in ethylene chloride were abandoned on account of the steeply inflected character of the mutarotation curve. But when using chloroform as the solvent, the inflexion disappears, and the curve resumes a normal appearance. We were fortunate in obtaining a specimen which changed very slowly, so that the action of light was easily detected. The results obtained were remarkable, and differed completely from those observed in the case of aminomethylenecamphor. Exposure to light at once stimulated the isomeric change, but the effects of the stimulus persisted after the light had been extinguished, so that the course of the curve was permanently deflected.* This acceleration was shown three times over on the same curve by repeated exposure of the solution to light (Fig. 4).

As it seemed possible that the permanent stimulus might be due to the liberation of a catalyst (say hydrogen chloride) from the chloroform used as solvent, the experiment was repeated with benzene as solvent, the readings being taken in this case with green mercury light. Precisely similar effects were observed. A solution which had not been exposed to light showed a very slow change of rotatory power. A second portion of the same solution showed the same initial rate of change, but was so stimulated by exposure to light during a period of forty minutes that the mutarotation was practically complete at the end of two more hours.

In the last experiments the only elements present in solvent and solute were carbon, hydrogen, and oxygen. The catalyst produced by the action of light must therefore be some purely "organic" compound, for example, an organic acid or ketone. Experiments in which benzoic acid was added to solutions of (enolic) benzoylcamphor in benzene showed a remarkable catalytic effect, the change being completed in about twenty minutes in the presence of a quantity of benzoic acid amounting only to 1 gram per litre of solution, or 2 per cent. of the weight of the solute. It is therefore

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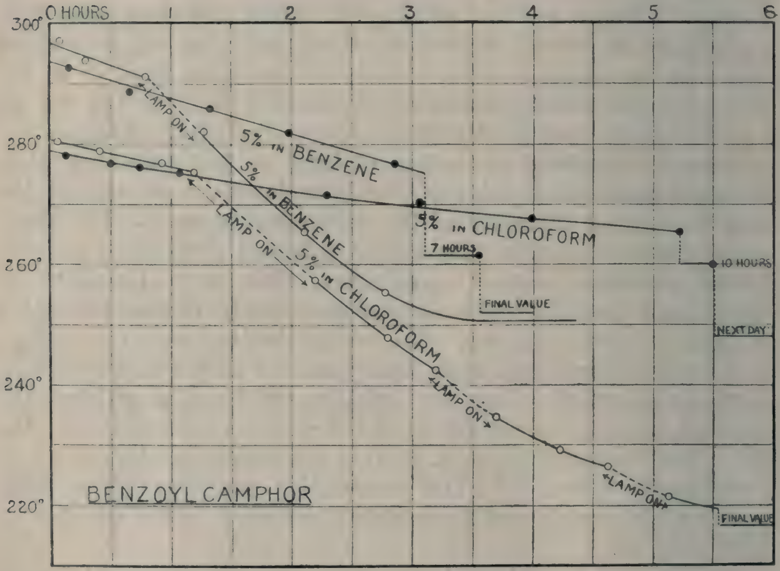
* These curves were plotted for sodium light as in Forster's experiments; all the others are for mercury-green light, wave-length 5461.

FIG. 4.

*Influence of light on the mutarotation of benzoylcamphor.*



very probable that the action of light on benzoylcamphor sets free small quantities of benzoic acid, and that the permanent stimulus to the isomeric change is due to the presence of this substance in the solutions.

## *Summary.*

1. Ultra-violet light does not accelerate the isomeric change of dextrose, galactose, or maltose, of nitrocamphor, or of hydroxymethylenecamphor.

2. In the case of aminomethylenecamphor there is a marked acceleration, which ceases when the stimulus is removed.

3. Benzoylcamphor also undergoes isomeric change more rapidly

in presence of light, but the acceleration persists after the light has been withdrawn. The permanent stimulus is probably due to the liberation of benzoic acid, which acts as a powerful catalyst in promoting isomeric change.

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## CXXVIII.—*The Estimation of Nitrites by means of Thiocarbamide, and the Interaction of Nitrous Acid and Thiocarbamide in the Presence of Acids of Different Strength.*

By May Emily Coade and Emil Alphonse Werner.

In a recent communication (Werner, T., 1912, **101**, 2180) it was pointed out that when a nitrite is added to an acid solution of thiocarbamide, the reaction may proceed in two directions, dependent entirely on the relative strength or ionising power of the acid present.

Thus, in presence of a feeble ioniser, such as acetic acid, the change takes place almost entirely in accordance with the following equation:

$$(a)\ CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O,$$

whilst if hydrochloric acid is present, the change is almost theoretically in agreement with equation (*b*):

$$(b)\ 2CSN_2H_4 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O.$$

In reaction (*a*) a small quantity of nitric oxide is always produced, and in reaction (*b*) the evolved gas contains a small proportion of nitrogen; this is of no importance so far as the estimation of nitrites is concerned, since the total volume of gas evolved is the same in both cases.

A few preliminary experiments seemed to indicate that thiocarbamide was likely to prove a useful substance for the estimation of various nitrites, and the results now recorded show beyond question that we have in this compound an admirable reagent for the simple, rapid, and accurate estimation of all nitrites by a gasometric method.

In carrying out these analyses, the following procedure was found to give very satisfactory results: a quantity of the nitrite, corresponding with a milligram-molecular proportion of nitrous acid together with 0·1 gram of thiocarbamide, was dissolved in 1 c.c. of water in the cup of the nitrometer, and introduced into the apparatus; an additional ½ c.c. of water was used to wash in the last traces from the cup; 1 c.c. of dilute acetic acid (20 per cent.) was then added. The reaction was completed in a few minutes. On account of the somewhat greater solubility of nitric oxide in water, as compared with nitrogen, it is preferable to use acetic acid.

A test experiment with pure silver nitrite gave a result in agreement with the theoretical; a sample of sodium nitrite gave for the mean of seven closely agreeing results a value equal to 96·76 per cent. of pure sodium nitrite; the same sample, when analysed by the well-known method, using ordinary carbamide, gave only 92·89 per cent. of pure sodium nitrite for the mean of three experiments, which were by no means so concordant as when thiocarbamide was used (Expts. 1—10).

An elegant volumetric method for the estimation of nitrites has been proposed by Rupp (*Zeitsch. anal. Chem.*, 1906, **45**, 690), based on the oxidation of the nitrite by a feebly alkaline solution of potassium permanganate, the excess of the latter, after five to ten minutes' heating on the water-bath, being determined by addition of potassium iodide, and after acidification, titrated with $N/10$-sodium thiosulphate. Two analyses of the sample of sodium nitrite by this method gave a mean value equal to 96·75 per cent. of pure nitrite, thus confirming the results obtained by the thiocarbamide method.

Estimations of ethyl nitrite in alcoholic solution have given results which appear to be more trustworthy than when the potassium iodide method is employed; with thiocarbamide, the values obtained were found to be always lower than those yielded by potassium iodide. This is due apparently to the presence of some nitric ester in the ethyl nitrite solution, which has a disturbing influence on the results obtained by the latter method, since a greater divergence was found in the values obtained from the analyses of an old specimen of the nitrous ester; the results of experiments 19 and 20 also appear to confirm this view.

The advantages which may be justly claimed for the estimation of nitrites by the aid of thiocarbamide are as follows:

(1) The accuracy of the results is not affected by the presence of nitrates, even when in large excess.

(2) The analysis can be completed in a few minutes, since no subsequent manipulation of the evolved gas is necessary, as in the case when ordinary carbamide is used; this also reduces the chances of experimental error.

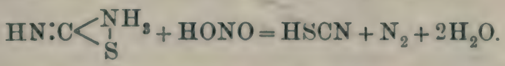
(3) The volume of gas evolved can be read off with great accuracy, since the operation is remarkably clean; even after a

large number of analyses the mercury remains quite untarnished, a result which is in marked contrast to that which occurs when potassium iodide is used after even a single operation.

(4) For the reasons given in (2) and (3), a much larger number of analyses can be made in a given time than by the other methods. For example, in the presence of sulphuric acid, the reaction is completed in about forty-five seconds; using acetic acid, it required only two minutes; in a comparative test, using carbamide in presence of sulphuric acid, the evolution of gas was not completed until after a lapse of twenty-eight minutes.

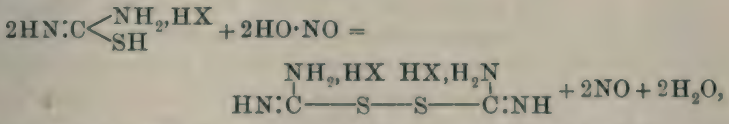
### *The Influence of Different Acids on the Composition of the Evolved Gas, when Nitrous Acid and Thiocarbamide interact.*

The following results furnish interesting confirmatory evidence in support of the theory which has recently been put forward by one of us (Werner, *loc. cit.*) to explain the sharp difference in the behaviour of nitrous acid towards thiocarbamide under the two conditions already referred to. In a neutral solution the thiocarbamide molecule is in a state of fairly stable equilibrium, represented by the configuration $HN\colon C\Big<\begin{matrix}NH_3\\ |\\ S\end{matrix}$, which is not disturbed by the presence of a feeble ioniser, such as acetic acid, with the result that the nitrous acid exerts a direct oxidising action on the thiocarbamide in accordance with the equation:

(*a*) 

$$HN\colon C\Big<\begin{matrix}NH_3\\ |\\ S\end{matrix} + HONO = HSCN + N_2 + 2H_2O.$$

When a strong acid is added, a salt of thiocarbamide is at once formed of the structure $HN\colon C\Big<\begin{matrix}NH_2,HX\\ SH\end{matrix}$, and oxidation by nitrous acid then takes place as follows:

(*b*) 

$$2HN\colon C\Big<\begin{matrix}NH_2,HX\\ SH\end{matrix} + 2HO\cdot NO =$$
$$\begin{matrix}NH_2,HX & & & & HX,H_2N & \\ | & & & & | & \\ HN\colon C & — & S & — S — & C\colon NH & \end{matrix} + 2NO + 2H_2O,$$

According to this view, the relative proportions of the two gases evolved should indicate the extent to which a particular acid was capable of reacting with thiocarbamide to form a salt, since interactions (*a*) and (*b*) will proceed simultaneously when both configurations of the thiocarbamide molecule are present in the solution.

In all the experiments, equal molecular proportions of thiocarbamide and sodium nitrite with two molecular proportions of the acid were allowed to interact in the same volume of solution;

the concentration of the thiocarbamide was therefore the same in each case; that of the acid varied somewhat according to the difference in molecular weight. For the latter reason it may be rightly argued that the experiments are not strictly comparable; still, the results recorded below prove conclusively that the direction of the change on the lines of equation (*b*) is directly proportional to the dissociation constant of the acid, a strong fact in support of the explanation just stated. The values in tables I and II have been calculated from the data given in the experimental part of this paper.

TABLE I.

| | NO, per cent. | $N_2$, per cent. |
|---|---|---|
| Hydrochloric acid ...... | 95·95 | 4·05 |
| Oxalic acid ...............<br>$(K=10)$ | 88·66 | 11·34 |
| Tartaric acid ......... ..<br>$(K=0{\cdot}108)$ | 58·01 | 41·99 |
| Malonic acid ...........<br>$(K=0{\cdot}163)$ | 51·88 | 48·12 |
| Malic acid ...............<br>$(K=0{\cdot}0395)$ | 39·68 | 60·32 |
| Lactic acid ..............<br>$(K=0{\cdot}0147)$ | 35·91 | 64·09 |
| Glycollic acid ...........<br>$(K=0{\cdot}0152)$ | 32·51 | 67·49 |
| Succinic acid ...........<br>$(K=0{\cdot}00655)$ | 19·37 | 80·63 |
| Acetic acid ...............<br>$(K=0{\cdot}0018)$ | 12·55 | 87·45 |
| Propionic acid .........<br>$(K=0{\cdot}0013)$ | 11·60 | 89·40 |

TABLE II.

| | NO, per cent. | $N_2$, per cent. |
|---|---|---|
| *o*-Bromobenzoic acid ... | 31·77 | 68·23 |
| *m*-Bromobenzoic acid..<br>$(K=0{\cdot}01307)$ | 18·16 | 81·84 |
| *p*-Bromobenzoic acid ... | 0·0 | 100·00 |
| *o*-Nitrobenzoic acid ...<br>$(K=0{\cdot}616)$ | 25·98 | 74·02 |
| *m*-Nitrobenzoic acid ...<br>$(K=0{\cdot}035)$ | 12·48 | 87·52 |
| *p*-Nitrobenzoic acid ...<br>$(K=0{\cdot}039)$ | 4·35 | 95·65 |

With the above derivatives of benzoic acid, it was necessary to use a certain amount of alcohol to help the solution of the acids, and in the case of the *p*-derivatives a larger volume was required than for the *o*- and *m*-compounds; the ionisation being thereby greatly diminished all round, the change has been diverted in the direction of equation (*a*) out of proportion to the dissociation constants of the acids. The larger volume of alcohol required in the case of *p*-nitrobenzoic acid, as compared with the meta-derivative, is no doubt the cause of the wide difference in the two results, which is also magnified by the influence of concentration, a factor the effect of which has yet to be studied. The result with *p*-bromobenzoic acid is remarkable as the only case in which nitrogen only was obtained; no record of its dissociation constant could be found.

Difference in concentration is probably also responsible for the order of the values obtained for malonic and tartaric acids, although the difference in constitution may also have some effect. It is intended to carry out further experiments to test these points.

## EXPERIMENTAL.

### *Estimation of Nitrites by means of Thiocarbamide.*

In order to establish the accuracy of the method, a specimen of freshly prepared silver nitrite, purified by recrystallisation from hot distilled water, was analysed, with the following result:

Silver nitrite (M.W. 153·9: 0·07695 gram) and thiocarbamide (0·1 gram) were introduced into the nitrometer with 2 c.c. of water, and 1 c.c. of acetic acid (20 per cent.) was added.

Vol. of gas evolved = 12 c.c. at 16·7° and 769·8 mm. = 11·24 c.c. (dry) at 0° and 760 mm.

Theoretical volume at N.T.P. = 11·18 c.c.

One gram of hydrogen, at N.T.P. = 11·18 litres, has been taken as the standard throughout all the experiments.

### *Analyses of Sodium Nitrite alone, and in the presence of Different Proportions of Sodium Nitrate.*

A sample of commercial pure fused sodium nitrite was used. 0·069 Gram of the sample and 0·1 gram of thiocarbamide were dissolved in 2 c.c. of water, and having been introduced into the nitrometer, 1 c.c. of dilute acetic acid (20 per cent.) was added. The reaction was completed in a few minutes. Theoretical volume of gas at N.T.P. = 22·36 c.c.:

| | Vol. at N.T.P. in c.c. | $NaNO_2$, per cent. |
|---|---|---|
| Expt. 1: | | |
| Gas evolved 23·5 c.c. at 17·4° and 758·82 mm....... | 21·64 | 96·84 |
| Expt. 2: | | |
| Gas evolved 23·5 c.c. at 16·6° and 757·5 mm. ...... | 21·66 | 96·87 |
| Expt. 3. 0·2 gram $NaNO_3$ present: | | |
| Gas evolved 23·8 c.c. at 17·6° and 750·5 mm. ...... | 21·66 | 96·87 |
| Expt. 4. 0·3 gram $NaNO_3$ present: | | |
| Gas evolved 23·4 c.c. at 16·7° and 760·35 mm....... | 21·65 | 96·82 |
| Expt. 5. 0·4 gram $NaNO_3$ present: | | |
| Gas evolved 23·9 c.c. at 18·8° and 750·55 mm....... | 21·61 | 96·64 |
| Expt. 6. 0·6 gram $NaNO_3$ present, also in Expt. 7: | | |
| Gas evolved 23·2 c.c. at 14·6° and 757·9 mm. ...... | 21·61 | 96·64 |
| Expt. 7: | | |
| Gas evolved 23·4 c.c. at 15·9° and 756·7 mm. ...... | 21·62 | 96·69 |

The presence of nitrates therefore does not materially affect the accuracy of the method, even when present to the extent of ten times the amount of the nitrite. This result is of importance in connexion with the use of thiocarbamide as a reagent for the estimation of nitrous esters, such as ethyl and amyl nitrites, which are liable to contain some of the corresponding nitric ester.

### *Comparative Analyses of the same sample of Sodium Nitrite by means of Carbamide.*

0·069 Gram of the sample of nitrite and 0·1 gram of carbamide were dissolved in 2 c.c. of water, and 1 c.c. of dilute sulphuric acid (1 in 7) was added; after absorption of the carbon dioxide by 1 c.c. of 30 per cent. potassium hydroxide solution, the following results were obtained:

| | Volume of gas ($N_2$). | Vol. at N.T.P. in c.c. | $NaNO_2$, per cent. |
|---|---|---|---|
| Expt. 8. | 22·9 c.c. at 13·2° and 733 mm. | 20·74 | 92·75 |
| Expt. 9. | 22·6 c.c. at 14·6° and 749·6 mm. | 20·81 | 93·07 |
| Expt. 10. | 23·0 c.c. at 14·1° and 733·5 mm. | 20·76 | 92·84 |

Mean of thiocarbamide results = 96·76 per cent. $NaNO_2$.
,, carbamide ,, = 92·89 ,, ,,

The results obtained with carbamide are beyond doubt too low, and this method is not trustworthy, as proved by the following analysis of the sodium nitrite by Rupp's method (*loc. cit.*).

*Expt.* 11.—0·069 Gram of sodium nitrite was dissolved in 40 c.c. of *N*/10-potassium permanganate solution, to which a few small crystals of sodium carbonate were added. The solution was warmed on the water-bath for fifteen minutes, cooled, acidified with dilute sulphuric acid, and excess of potassium iodide then added; the liberated iodine was titrated with *N*/10-sodium thiosulphate.

20·7 c.c. *N*/10-$Na_2S_2O_3,5H_2O$ required. Hence $40-20·7=19·3$ c.c. *N*/10-$K_2Mn_2O_8$ required for oxidation of the nitrite. (1 c.c. = 0·00345 $NaNO_2$) = 96·5 per cent. $NaNO_2$.

Another experiment gave as a result 97 per cent. $NaNO_2$, thus confirming the accuracy of the experiments with thiocarbamide.

### *Analyses of Ethyl Nitrite in Alcoholic Solution.*

A dilute solution of ethyl nitrite was prepared according to the method described in the British Pharmacopœia, which yields a product containing as nearly as possible 2·5 per cent. of the pure ester. One c.c. of this solution should give, when analysed by the well-known method using potassium iodide, 7 c.c. of gas (NO) at 15·5° and 760 mm.

Results using thiocarbamide, 1 c.c. of ethyl nitrite solution, 0·1 gram of thiocarbamide, dissolved in 1 c.c. of water, 1 c.c. of dilute acetic acid:

| | Gas evolved. | Vol. (c.c.) at 15·5° and 760 mm. |
|---|---|---|
| Expt. 12. | 6·9 c.c. at 11·7° and 758 mm. | 6·88 |
| Expt. 13. | 6·9 c.c. at 12·1° and 758 mm. | 6·87 |

Estimated by the potassium iodide method, 1 c.c. of 10 per cent. potassium iodide solution, 1 c.c. of dilute sulphuric acid:

| | | |
|---|---|---|
| Expt. 14. | 7 c.c. at 11·2° and 758 mm. .............. | 6·99 |

In order to obtain a further comparison of the two methods, a specimen of "sweet spirits of nitre" several months old was analysed, with the following results (2 c.c. of the sample were taken in each experiment):

### *A*.—Thiocarbamide Method.

| | Gas evolved. | Vol at N.T.P. in c.c. |
|---|---|---|
| Expt. 15. | 4·6 c.c. at 14·6° and 751 mm................ | 4·24 |
| Expt. 16. | 4·5 c.c. at 14·6° and 751 mm................ | 4·15 |

### *B*.—Potassium Iodide Method.

| | | |
|---|---|---|
| Expt. 17. | 4·9 c.c. at 14·6° and 771·7 mm. ......... | 4·65 |
| Expt. 18. | 4·9 c.c. at 14·7° and 760·85 mm. ......... | 4·58 |

The greater divergence in the results by the two methods with the old specimen of the nitrite solution suggests that the accuracy of the potassium iodide method is probably affected by the presence of some ethyl nitrate in the sample, and the following results of the analysis of sodium nitrite in presence of some sodium nitrate appear to confirm this view.

0·069 Gram of sodium nitrite and 0·138 gram of sodium nitrate (that is, double the weight of the nitrite) were dissolved in 2 c.c. of water; 2 c.c. of potassium iodide solution were added, and having been introduced into the nitrometer, 2 c.c. of dilute sulphuric acid were added:

| | Gas evolved. | Vol. at N.T.P. in c.c. | $NaNO_2$, per cent. |
|---|---|---|---|
| Expt. 19. | 23·3 c.c. at 15·3° and 765·35 mm. ...... | 21·84 | 97·6 |
| Expt. 20. | 23·4 c.c. at 16·2° and 762·8 mm. ......... | 21·78 | 97·4 |

The mean result of these two determinations, namely, 97·5, is thus 0·74 per cent. higher than that obtained for the same specimen of sodium nitrite when analysed by the aid of thiocarbamide (see after Expt. 10), or by Rupp's method (*loc. cit.*). An alcoholic solution of commercial pure amyl nitrite was also found to give a somewhat higher result when analysed by means of potassium iodide, as compared with the thiocarbamide method.

### *Analyses of the Gases Evolved when Nitrous Acid and Thiocarbamide interact in the presence of Acids of Different Strength and Constitution.*

In all the following experiments a milli-molecular proportion of thiocarbamide (0·076) and two milli-molecular proportions of the acid were dissolved in about 2 c.c. of water and introduced into the nitrometer; 0·072 gram of sodium nitrite (equivalent to 0·069 of the pure salt) dissolved in 1 c.c. of water was then added.

After the evolution of gas had ceased, the volume was read off, and the nitric oxide was then absorbed by means of a fresh saturated solution of ferrous sulphate; the residual nitrogen was measured after complete absorption of the nitric oxide was ensured. Since the object in these experiments was merely to determine the relative proportions of the two gases evolved, the volume results obtained, corrected to the normal temperature and pressure, are alone given. The theoretical volume of the mixed gases is 22·36 c.c.:

| Expts. 21—36. | Vol. at N.T.P. in c.c. | Vol. of NO. | Vol. of nitrogen. |
|---|---|---|---|
| Hydrochloric acid | 22·37 | 21·47 | 0·9 |
| Oxalic acid | 22·41 | 19·87 | 2·54 |
| Malonic acid | 21·36 | 11·08 | 10·28 |
| Succinic acid | 22·16 | 4·29 | 17·87 |
| Malic acid | 22·25 | 8·83 | 13·42 |
| Tartaric acid | 22·36 | 12·97 | 9·39 |
| Acetic acid | 22·39 | 2·88 | 19·51 |
| Propionic acid | 22·42 | 2·60 | 19·82 |
| Glycollic acid | 22·49 | 7·30 | 15·19 |
| Lactic acid | 22·39 | 8·04 | 14·35 |
| *o*-Nitrobenzoic acid | 21·21 | 5·51 | 15·70 |
| *m*-Nitrobenzoic acid | 22·04 | 2·75 | 19·29 |
| *p*-Nitrobenzoic acid | 18·42 | 0·80 | 17·62 |
| *o*-Bromobenzoic acid | 21·06 | 6·69 | 14·37 |
| *m*-Bromobenzoic acid | 20·03 | 3·69 | 16·63 |
| *p*-Bromobenzoic acid | 22·63 | 0·00 | 22·63 |

In the experiments with the derivatives of benzoic acid, 2 c.c. of alcohol were used as solvent for the *o*- and *m*-compounds, and 4 c.c. for the *p*-compounds, on account of the sparing solubility of these acids in water; even then the reactions were not quite completed. The evolution of gas was very slow; twenty-four hours were required in the case of *p*-bromobenzoic acid. The results, however, show sufficiently the effects of these acids on the direction of the change.

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## CXXIX.—*Sylvestrene. The Constitution of* d-*Sylvestrene and its Derivatives.*

By WALTER NORMAN HAWORTH, WILLIAM HENRY PERKIN, jun., and OTTO WALLACH.

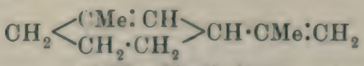
DURING his researches on Swedish oil of turpentine, Atterberg (*Ber.*, 1877, **10**, 1202; 1878, **11**, 1698) made the important discovery that this oil contains, besides pinene, a new terpene which boils at 173—175°, and to which he gave the name *sylvestrene*. He showed that this terpene combines with two molecules of hydrogen chloride to yield sylvestrene dihydrochloride, $C_{10}H_{16},2HCl$, which melts at 72°, and is so characteristic that its formation is one of the best means of identifying sylvestrene. At a later date, Wallach (*Annalen*, 1885, **230**, 241; 1887, **239**, 24; 1888, **245**, 272) also investigated Swedish oil of turpentine, and was able to confirm Atterberg's results in every particular; he also prepared the dihydrobromide, $C_{10}H_{16},2HBr$ (m. p. 72°), the dihydriodide, $C_{10}H_{16},2HI$ (m. p. 66—67°), the tetrabromide, $C_{10}H_{16}Br_4$ (m. p. 135—136°), and the nitrosochloride, $C_{10}H_{16}NOCl$ (m. p. 106—107°). By the decomposition of the pure dihydrochloride by means of potassium hydroxide or aniline, Wallach obtained an oil which did not boil constantly, and from which, by repeated fractionation, he isolated a specimen of sylvestrene, which had the following properties:

$$\text{B. p. } 175\text{—}176°;\ d_{20}\ 0{\cdot}848°;\ n_D\ 1{\cdot}47573;\ \alpha_D\ +66{\cdot}32°,$$

and, as these properties were very similar to those of *d*-limonene, he suggested that sylvestrene probably belonged to the same group.

During the above fractionation the presence of a considerable quantity of a terpene of higher boiling point was observed, but this was at that time not further investigated.

Subsequently Baeyer (*Ber.*, 1894, **27**, 3488, 3491; 1898, **31**, 1067, 1070) showed that sylvestrene is converted, by exhaustive bromination, into *m*-cymene, and that it therefore belongs to the group of the *m*-menthadienes; he expressed the opinion that carvestrene, which he had prepared from carone and which also belongs to the *m*-series, is the *dl*-modification of sylvestrene. Baeyer also suggested that the expression

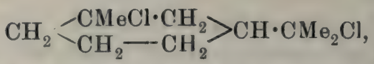


$$CH_2{<}\begin{matrix}CMe{:}CH\\CH_2{\cdot}CH_2\end{matrix}{>}CH{\cdot}CMe{:}CH_2$$

$\Delta^{1:8(9)}$-*m*-Menthadiene.

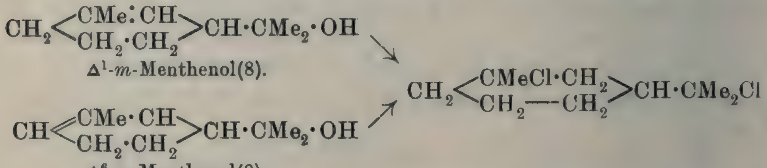
most probably represent both carvestrene and sylvestrene, but he did not bring forward any sufficient evidence that the double linking actually occupies the position assigned to it in this formula.

We have been engaged for some years on a series of experiments undertaken with the object of supplying a definite proof of the structure of sylvestrene, but the problem has proved to be a very difficult one. In the first place, Swedish oil of turpentine contains, besides sylvestrene, other terpenes boiling approximately at the same temperature, and it is therefore not possible to isolate sylvestrene from this oil by fractional distillation and directly to determine its properties. In order to obtain the sylvestrene, it is necessary to convert the fraction of the terpenes boiling at 173—178° into the dihydrochlorides, to isolate the characteristic sylvestrene dihydrochloride by recrystallisation, and then to decompose this by bases in the usual manner. It has long been assumed that this dihydrochloride has the constitution represented by the formula:



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CMeCl{\cdot}CH_2}\\ \mathrm{CH_2{-}{-}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CMe_2Cl},$$

but the first proof of this was the observation that *dl*-$\Delta^1$-*m*-menthenol(8) (Perkin and Tattersall, T., 1907, **91**, 481) and *dl*-$\Delta^6$-*m*-menthenol(8) (Fisher and Perkin, T., 1908, **93**, 1888) both yield carvestrene dihydrochloride on treatment with hydrochloric acid:



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CMe_2{\cdot}OH} \searrow$$

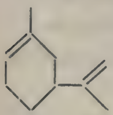
$\Delta^1$-*m*-Menthenol(8).

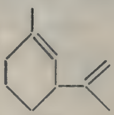
$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CMeCl{\cdot}CH_2}\\ \mathrm{CH_2{-}{-}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CMe_2Cl}$$

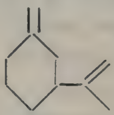
$$\mathrm{CH}{\ll}\begin{matrix}\mathrm{CMe{\cdot}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CMe_2{\cdot}OH} \nearrow$$

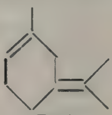
$\Delta^6$-*m*-Menthenol(8).

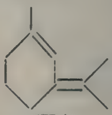
and, further, that *d*-$\Delta^6$ *m*-menthenol(8) is converted by hydrochloric acid into sylvestrene dihydrochloride, which is thus proved to be the *d*-constituent of carvestrene dihydrochloride (Perkin, P., 1910, **26**, 97).* Although the constitution of sylvestrene dihydrochloride may now be considered as definitely established, this is not the case with sylvestrene itself, because it is obvious that the following terpenes might result from the elimination of two molecules of hydrogen chloride from sylvestrene dihydrochloride:

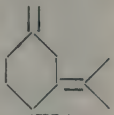

(I.)


(II.)


(III.)


(IV.)


(V.)


(VI.)

Of these, (IV), (V), and (VI) are out of the question, because they represent inactive configurations, whilst sylvestrene is active, and formula III, although it must be taken into account, is nevertheless highly improbable, because it does not account in a satisfactory manner for several of the properties of sylvestrene; it follows, therefore, that the two formulæ which require the most careful consideration are I and II.

The principal difficulty in investigating this matter is the long and tedious preparation of sylvestrene dihydrochloride from Swedish oil of turpentine which can hardly be carried out on a sufficient scale in ordinary laboratory apparatus. Fortunately, during the last few years, Messrs. Schimmel & Co. have undertaken the preparation of relatively large quantities of sylvestrene dihydrochloride, and have generously placed at our disposal a considerable amount of this valuable material. We take this opportunity of thanking Messrs. Schimmel for their generous assistance, without which the present investigation could hardly have been attempted. The main objects which we have had in view during this series of experiments have been similar to those pursued by Wallach in his investigation of the other terpene dihydrochlorides, namely, the preparation and investigation of the hydrocarbon mixture obtained by the elimination of hydrogen chloride from sylvestrene dihydrochloride and of the sylveterpineols and sylveterpins which result from the action of alkalis on this dihydrochloride.

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* This matter will be discussed more fully in Part II of this investigation.

### *Sylvestrene from Sylvestrene Dihydrochloride.*

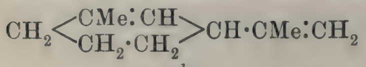
It has already been mentioned that Wallach had observed in 1885 that the substance obtained from sylvestrene dihydrochloride by the action of bases did not distil at a constant temperature, but he ultimately succeeded in isolating a fraction boiling at 175—176° which had $\alpha_D$ +66·32°. The subsequent development of the chemistry of the terpenes has made it clear that a single substance is not to be expected as the result of this elimination of hydrogen chloride, since, although the possibility of the formation of isomerides in the *p*-series is not so great as in the *m*-series, experiment has shown that the hydrocarbons formed by the removal of hydrogen chloride from dipentene and terpinene dihydrochlorides are always mixtures. We have now very carefully investigated this matter, and have submitted a large quantity of the mixture of terpenes resulting from the action of diethylaniline on pure sylvestrene dihydrochloride and subsequent distillation in steam, to very careful fractionation with a Young column. After the third fractionation, an oil was collected, which distilled at 174—176°, and has $\alpha_D$ +66·05°, but, as the fractionations were continued, the values for $\alpha_D$ continually rose until at the tenth operation a hydrocarbon was obtained which distilled at 175°/751 mm. and had the high value $\alpha_D$ +83·18° at 18°. The quantity had then become too small for further fractionation. The physical properties of this fraction were as follows: $d_{18}$ 0·8479°; $n_D$ 1·4760; M 45·24 (calc. for $C_{10}H_{16}|^{-2}$ 45·24), and, with the exception of the higher rotation, these values correspond closely with those previously found by Wallach for the fraction 175—176°, namely, $d_{20}$ 0·848°; $n_D$ 1·4757, and $\alpha_D$ +66·32°.

We next carefully examined a considerable quantity of the higher fractions which had accumulated, and, as the result of a large number of fractionations, succeeded in isolating an oil which distilled at 182—184°/755 mm., and gave the following results on analysis:

0·1587 gave 0·5716 $CO_2$ and 0·1692 $H_2O$. C=87·9; H=11·8.

$C_{10}H_{16}$ requires C=88·2; H=11·8 per cent.

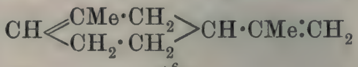
The physical properties of this fraction were the following: $d_{17}$ 0·870; $n_D$ 1·4896; M 45·16; and $\alpha_D$ +45·42°. It will be observed that the values for $d$ and $n_D$ are considerably higher than those of the fraction 175°, whereas $\alpha_D$ is much lower. The oil distilling at 182—184° resinifies readily in contact with air, and also on distillation over sodium, and, when it is mixed with a saturated solution of hydrogen chloride in glacial acetic acid, it yields a large crop of crystals of sylvestrene dihydrochloride. It is probable that this fraction contains a considerable proportion of inactive sylveterpinolene (p. 1237) mixed with some isomeride of similar boiling point, but having a high rotation. There is reason to believe that the fraction of boiling point 175° and rotation +83·18° is still not a single substance, but is a mixture of the $\Delta^1$- and $\Delta^6$-isomerides



$CH_2<\begin{matrix}CMe{:}CH\\CH_2\cdot CH_2\end{matrix}>CH\cdot CMe{:}CH_2$

$\Delta^1$-.

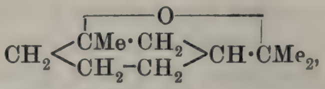
and



$CH<\begin{matrix}CMe\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CMe{:}CH_2$

$\Delta^6$-.

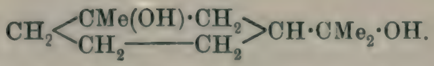
(compare p. 1230), and this point will be more fully discussed in Part II of this investigation. It may here be stated that several experiments were made in the endeavour to obtain a sylvestrene of definite constitution from sylveterpin by the elimination of water under different conditions, but without success. The reason for the failure lies in the fact that this dihydroxy-derivative of sylvestrene exhibits a marked tendency to lose water with the formation of *m*-cineole:



$CH_2<\begin{matrix}CMe\cdot CH_2\\CH_2{-}CH_2\end{matrix}>CH\cdot CMe_2,$

which cannot be separated from the terpene, and even a small quantity of which has a marked influence on its physical properties. During the course of their experiments on the synthesis of carvestrene, Perkin and Tattersall (T., 1907, **91**, 485, 503) isolated *dl*-*m*-cineole from the products of the action of magnesium methyl iodide on ethyl *cyclo*hexanone-3-carboxylate, and showed that it distilled at 177—178°, so that it would be impossible to separate a mixture of this substance and sylvestrene by fractional distillation.

### *α- and β-Sylveterpin*,

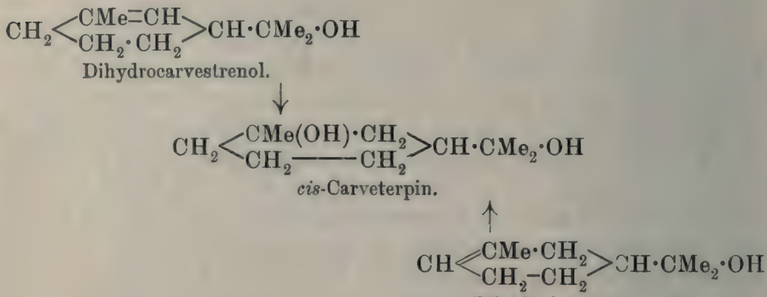


$$CH_2{<}\begin{matrix}CMe(OH)\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}{>}CH\cdot CMe_2\cdot OH.$$

During the course of the earlier investigations on sylvestrene dihydrochloride (Wallach, *Annalen*, 1907, **357**, 73), it was shown that an unsaturated alcohol (sylveterpineol, compare p. 1234) and a terpin (sylveterpin) are produced when the dihydrochloride is shaken with dilute aqueous potassium hydroxide. At that time, however, the terpin was isolated only as one modification melting at 136°. Further experiments have shown that besides this, a second modification is also produced during the action of dilute potassium hydroxide on sylvestrene dihydrochloride, which is much more soluble and melts at a lower temperature. In order to isolate this, the crude terpin obtained in the manner already described (*loc. cit.*), which melts roughly at 50—60° and distils at 144°/16 mm., is dissolved in benzene, and fractionally precipitated by light petroleum. During this process the α-sylveterpin of higher melting point separates first, and this after recrystallisation melts at 137—138°, and is dextrorotatory, the solution in chloroform having $\alpha_D$ +27·74°; it sublimes readily, even on the steam-bath. The mother liquors contain the modification of lower melting point, and, on account of the sticky impurities which are present and very difficult to remove, the isolation of this β-sylveterpin in a pure condition is a very troublesome matter. After repeated fractional crystallisation it was found to melt at 70—75°, and have $\alpha_D$ +20·93° (in chloroform) and +18·48° in methyl alcohol. It was subsequently found that both modifications are produced when sylveterpineol is shaken with dilute sulphuric acid for several days. In this experiment sylveterpineol (compare p. 1234) (8 grams) was shaken on the machine with sulphuric acid (6 grams) and water (600 c.c.) for several days, the product neutralised with sodium carbonate, and, after the unchanged sylveterpineol had been removed by distillation in steam, the residue was several times extracted with chloroform. After the chloroform had been removed by evaporation, a syrupy mass was obtained, which, when rubbed with light petroleum, soon crystallised, and, after the substance had been left in contact with porous porcelain until quite dry, it was separated into the *cis*- and *trans*-(β- and α-)modifications of sylveterpin by fractional crystallisation in the manner just described.

It follows from these experiments that the sylvestrene derivatives yield *cis*- and *trans*-terpins under exactly the same conditions as the corresponding derivatives in the para-series.

The *cis*- and *trans*-modifications of sylveterpin are the *d*-constituents of the *cis*- and *trans*-carveterpins (tetrahydrocarvestrenediols), the former of which (*cis*-) melts at 90°, and was first prepared by Perkin and Tattersall (T., 1907, **91**, 501) from dihydrocarvestrenol, and subsequently by Fisher and Perkin (T., 1908, **93**, 1889) from dihydro*iso*carvestrenol, in both cases by the action of dilute sulphuric acid:



$$\mathrm{CH_2}\left<\begin{array}{c}\mathrm{CMe{=}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}\right>\mathrm{CH\cdot CMe_2\cdot OH}$$

Dihydrocarvestrenol.

$$\downarrow$$

$$\mathrm{CH_2}\left<\begin{array}{c}\mathrm{CMe(OH)\cdot CH_2}\\ \mathrm{CH_2 \text{———} CH_2}\end{array}\right>\mathrm{CH\cdot CMe_2\cdot OH}$$

*cis*-Carveterpin.

$$\uparrow$$

$$\mathrm{CH}\left<\begin{array}{c}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2{-}CH_2}\end{array}\right>\mathrm{CH\cdot CMe_2\cdot OH}$$

Dihydro*iso*carvestrenol.

*trans*-Carveterpin melts at 126—127°, and was first described by Baeyer (*Ber.*, 1894, **27**, 3490), who obtained it from carvestrene dihydrobromide by the action of silver acetate, and then of methyl-alcoholic potassium hydroxide. When *trans*-sylveterpin (6 grams) was digested in an apparatus provided with an efficient condenser, with permanganate (7·4 grams) dissolved in water (220 c.c.) for fifteen minutes, and the volatile products distilled off, the distillate gave the iodoform reaction, and, on treatment with phenylsemicarbazide, the phenylsemicarbazone of acetone was obtained, melting at 154—155°, showing that acetone is a product of the oxidation of *trans*-sylveterpin under these conditions.

### *Sylveterpineol* (*Sylvestrol*), $C_{10}H_{17}\cdot OH$.

This important derivative, which is obtained as the principal product, together with sylveterpin and about 5 per cent. of hydrocarbon, when sylvestrene dihydrochloride is shaken with dilute potassium hydroxide (compare Wallach, *Annalen*, 1907, **357**, 74) distils at 214°, and has $d$ 0·924; $n_D$ 1·4822 at 22°; M 47·53 (calc., 47·96), and $\alpha_D$ +45·9°.

It was also shown that this unsaturated alcohol is oxidised by dilute permanganate, with formation of the corresponding glycerol, $C_{10}H_{17}(OH)_3$, which was obtained as a viscid syrup, and distilled at 165°/11 mm. It has now been found that this syrup partly crystallises when it is rubbed with light petroleum and allowed to remain in a desiccator, and, after contact with porous porcelain, the solid residue was purified by recrystallisation from a mixture of acetic ester and light petroleum. The sylveglycerol thus obtained melted at 105°, and gave the following results on analysis:

0·1170 gave 0·2740 $CO_2$ and 0·1130 $H_2O$. C=63·8; H=11·0.
$C_{10}H_{20}O_3$ requires C=63·8; H=10·7 per cent.

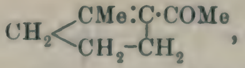
Since the original syrupy glycerol gave results on analysis (*loc. cit.*) which agreed closely with the formula $C_{10}H_{20}O_3$, it is clear that it consists of a mixture of isomeric glycerols, but the nature of these could not be determined. When the crude glycerol is warmed with dilute sulphuric acid, a ketone is formed which has the odour of menthone, and yields a semicarbazone melting at 190—192°, and at the same time a hydrocarbon is produced which has the odour of cymene, distils at 177°, and doubtless consists of *m*-cymene.

During the oxidation of sylveterpineol with permanganate other substances besides the glycerol just described are produced, and as their nature seemed likely to afford evidence of the constitution of the terpineol these have been carefully investigated.

Sylveterpineol, in portions of 6 grams, was mixed with powdered ice and oxidised at 0° by the gradual addition of a solution of 8·2 grams of permanganate in 300 c.c. of water, the whole being well stirred during the operation. As soon as the oxidation, which takes about an hour, was complete, the filtrate from the manganese precipitate was saturated with carbon dioxide, distilled in steam (*A*), and the distillate mixed with ammonium sulphate and extracted with ether. After drying and evaporating, a small quantity of an oil was obtained, which had the odour similar to that of camphor and *cyclo*hexanone, and distilled at 185—190°:

0·1002 gave 0·2836 $CO_2$ and 0·0917 $H_2O$. C=77·3; H=10·1.
$C_8H_{12}O$ requires C=77·4; H=9·7 per cent.

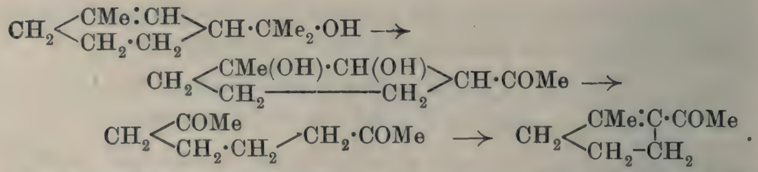
There can be little doubt that this ketone is 2-acetyl-1-methyl-$\Delta^1$-*cyclo*pentene,



$$CH_2<\begin{matrix}CMe:C\cdot COMe\\ \quad\;\; | \\ CH_2-CH_2\end{matrix},$$

because it yields a semicarbazone, which is sparingly soluble in alcohol, melts at 220°, and the mixture of which with the semicarbazone of acetylmethyl*cyclo*pentene (T., 1908, **93**, 1946; *Ber.*, 1909, **42**, 146) melts at the same temperature.

This formation of acetylmethyl*cyclo*pentene is evidently due, in the first place, to the oxidation of sylveterpineol to diacetylbutane, which, as Marshall and Perkin (T., 1890, **57**, 242) have shown, very readily undergoes internal condensation with the formation of methyldihydropentene methyl ketone (acetylmethyl*cyclo*pentene):



$$CH_2{<}\begin{array}{l}CMe{:}CH\\CH_2{\cdot}CH_2\end{array}{>}CH{\cdot}CMe_2{\cdot}OH \rightarrow$$

$$CH_2{<}\begin{array}{l}CMe(OH){\cdot}CH(OH)\\CH_2\text{————}CH_2\end{array}{>}CH{\cdot}COMe \rightarrow$$

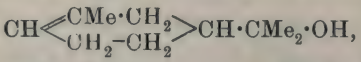
$$CH_2{<}\begin{array}{l}COMe\\CH_2{\cdot}CH_2{\diagup}CH_2{\cdot}COMe\end{array} \rightarrow CH_2{<}\begin{array}{l}CMe{:}C{\cdot}COMe\\CH_2{-}CH_2\end{array}.$$

The alkaline residue from the steam distillation (A) was first extracted with ether in the Hagemann continuous extraction apparatus in order to remove neutral substances, then acidified with hydrochloric acid, and again extracted in the same apparatus. After drying, the ethereal solution was evaporated, and the yellow, syrupy residue heated at 100° for two hours in order to convert as much as possible of the ketohydroxy-acid, which was evidently present, into the corresponding lactone. The product was dissolved in ether, the ethereal solution extracted with sodium carbonate to remove any acid present, dried over potassium carbonate, evaporated, and the residue fractionated, when the greater portion distilled at 175°/25 mm., and gave the following analytical results:

0·1077 gave 0·2570 $CO_2$ and 0·0874 $H_2O$. C=65·1; H=9·0.

$C_{10}H_{16}O_3$ requires C=65·2; H=8·7 per cent.

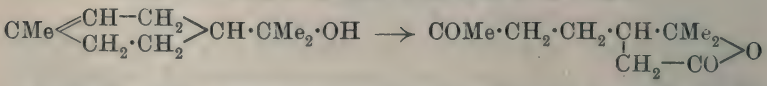
*Titration.*—0·1434 Gram was dissolved in excess of warm *N*/10-NaOH and titrated back with *N*/10-$H_2SO_4$, when it was found that 0·0316 gram NaOH was required for neutralisation, whereas this quantity of a keto-lactone should neutralise 0·0312 gram. The presence of the acetyl group in the lactone is indicated by the fact that it yields iodoform when its solution in sodium hydroxide is treated with iodine, and there can be little doubt that it is the product of the oxidation of $\Delta^6$-*m*-menthenol(8),



$$CH{<}\begin{array}{l}CMe{\cdot}CH_2\\CH_2{-}CH_2\end{array}{>}CH{\cdot}CMe_2{\cdot}OH,$$

one of the constituents of sylveterpineol. Wallach (*Annalen*, 1893, **275**, 153) has shown that ordinary terpineol yields the γ-lactone of ε-keto-β-hydroxy*iso*propylheptoic acid,

$Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CMe_2{\cdot}OH){\cdot}CH_2{\cdot}CO_2H$,

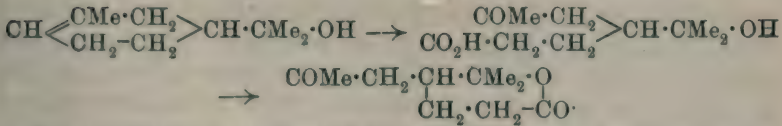


$$CMe{<}\begin{array}{l}CH{-}CH_2\\CH_2{\cdot}CH_2\end{array}{>}CH{\cdot}CMe_2{\cdot}OH \rightarrow \begin{array}{l}COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CMe_2\\ \qquad\qquad\qquad\quad CH_2{-}CO\end{array}{>}O$$

on oxidation with permanganate (compare also the formation of the lactone of α-methyl-γ-hydroxy*iso*propyladipic acid from $\Delta^5$-*m*-menthenol(8), T., 1910, **97**, 2132). In the present case the oxidation evidently proceeds with the formation of the δ-lactone of ε-keto-γ-hydroxy*iso*propylheptoic acid,

$Me{\cdot}CO{\cdot}CH_2{\cdot}CH(CMe_2{\cdot}OH){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$,

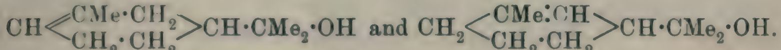
according to the scheme:



$$\mathrm{CH}<\begin{matrix}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2{-}CH_2}\end{matrix}>\mathrm{CH\cdot CMe_2\cdot OH} \longrightarrow \begin{matrix}\mathrm{COMe\cdot CH_2}\\ \mathrm{CO_2H\cdot CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe_2\cdot OH}$$

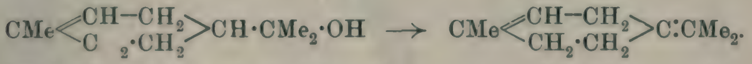
$$\longrightarrow \begin{array}{l}\mathrm{COMe\cdot CH_2\cdot CH\cdot CMe_2\cdot O}\\ \qquad\qquad\quad \mathrm{CH_2\cdot CH_2{-}CO}\end{array}$$

The formation of this δ-ketolactone, on the one hand, and of 2-acetylmethyl*cyclo*pentene on the other, seems to us to prove conclusively that the sylveterpineol obtained by the action of dilute alkalis on sylvestrene dihydrochloride is a mixture of $\Delta^6$-*m*-menthenol(8) and $\Delta^1$-*m*-menthenol(8):



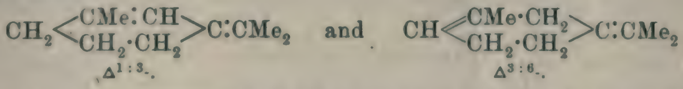
$$\mathrm{CH}<\begin{matrix}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe_2\cdot OH} \text{ and } \mathrm{CH_2}<\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe_2\cdot OH.}$$

*Action of Oxalic Acid on Sylveterpineol.*—Wallach and Kerkhoff (*Annalen*, 1893, **275**, 107) and Baeyer (*Ber.*, 1894, **27**, 448) have shown that ordinary terpineol loses water with formation of terpinolene and some cineole when it is digested with aqueous oxalic acid:



$$\mathrm{CMe}<\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe_2\cdot OH} \longrightarrow \mathrm{CMe}<\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{:}CMe_2.}$$

With the object of studying the corresponding decomposition in the *m*-series, sylveterpineol was digested with 15 per cent. aqueous oxalic acid, the oily layer separated and fractionated, when a hydrocarbon was isolated, which distilled at 185° and was almost inactive. When this hydrocarbon was freshly distilled and at once analysed, it gave results somewhat too low for those required by the formula $C_{10}H_{16}$, due doubtless to the presence of *m*-cineole, and on keeping for a few hours it had absorbed oxygen and commenced to resinify. It is probable that this substance contains a mixture of the two *m*-terpinolenes:



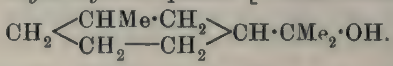
$$\underset{\Delta^{1:3}.}{\mathrm{CH_2}<\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{:}CMe_2}} \quad \text{and} \quad \underset{\Delta^{3:6}.}{\mathrm{CH}<\begin{matrix}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{:}CMe_2}}$$

and evidence in support of this view was supplied by the observation that, when the mixture is treated with hydrogen chloride, it yields *dl*-sylvestrene dihydrochloride (carvestrene dihydrochloride), melting at 50—52°.

*Conversion of Sylveterpineol into* m-*Cymene.*—This change may be readily accomplished in the following manner: Sylveterpineol (10 grams), dissolved in glacial acetic acid (25 c.c.) and cooled at 0°, is gradually mixed with bromine (3·3 c.c.) and cautiously heated by a small flame.

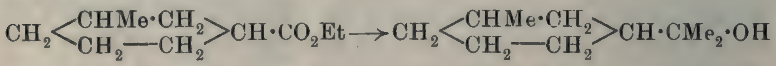
In a short time evolution of hydrogen bromide commences, and is almost complete in about an hour; the product is, however, boiled for some hours, neutralised with alkali, and distilled in steam until no more oil passes over. The distillate is mixed with ice, and shaken with permanganate until the colour remains; it is then again distilled, and the oil separated and distilled over sodium. In this way 5·8 grams of an oil were obtained, which boiled constantly at 175—176°, and, when oxidised with permanganate under the conditions recommended by Wallach (*Annalen*, 1893, **275**, 159), yielded *m*-hydroxy*iso*propylbenzoic acid, melting at 123—124°. The oil was therefore *m*-cymene.

### *d*(3)[*]-*Dihydrosylveterpineol* [d-m-*Menthanol*(8)],



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{matrix}>CH\cdot CMe_2\cdot OH.$$

During the course of a series of experiments on the reduction of alicyclic compounds (*Annalen*, 1911, **381**, 60) Wallach showed that sylveterpineol, on reduction at the ordinary temperature with hydrogen in the presence of colloidal palladium under the conditions recommended by Paal (compare *Ber.*, 1905, **38**, 1398), yields a dihydrosylveterpineol, which distils at 206—208°, gives a phenylurethane melting at 71—74°, and is presumably structurally identical with the *dl-m*-menthanol(8), which Perkin and Tattersall (T., 1905, **87**, 1102) had previously obtained from ethyl hexahydro-*m*-toluate (ethyl 1-methyl*cyclo*hexane-3-carboxylate) by the action of magnesium methyl iodide:



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{matrix}>CH\cdot CO_2Et\longrightarrow CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$$

and which distilled at 102°/20 mm. The dihydrosylveterpineol from sylveterpineol is, however, optically active, and has $\alpha_D$ +10·35°, and the following analytical and synthetical experiments prove conclusively that it has the constitution assigned to it at the head of this section.

*Oxidation of* d(3)-*Dihydrosylveterpineol by Chromic Acid to Acetone and* dl-1-*Methyl*cyclo*hexan*-3-*one*.[†]—After several preliminary experiments, the conditions which were found to give the most satisfactory results were the following. The dihydrosylveterpineol (3 grams) was dissolved in glacial acetic acid (10 c.c.), heated on the water-bath, and then a solution of chromic acid (6 grams) in water (3 c.c.) added drop by drop, when a vigorous reaction set in, causing the liquid to boil without any further external heat, and the process was finished in about ten minutes. The product was diluted with water, neutralised with sodium carbonate, and distilled in steam, when an oil was obtained which yielded a crystalline semicarbazone (0·8—1 gram), and 15 grams of this derivative were prepared. On examination this proved to be unusually soluble in water and a mixture; the ketone was therefore regenerated and fractionated, the portion distilling at 170—172° being separately collected. This fraction contained an unsaturated substance, which was removed by permanganate, and the saturated ketone then yielded a semicarbazone, which, after crystallisation from a mixture of methyl alcohol and ether, melted at 186°:

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[*] The number in brackets indicates the position of the asymmetric carbon atom to which optical activity is due.

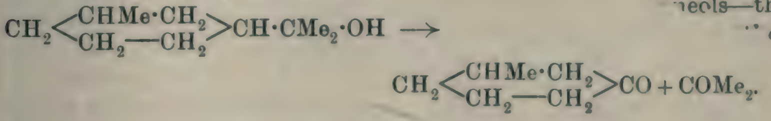
[†] We are much indebted to Dr. Walther Ost for valuable assistance during the course of these experiments.

0·1993 gave 0·4133 $CO_2$ and 0·1596 $H_2O$. C=56·5; H=9·0.

$C_8H_{15}ON_3$ requires C=56·7; H=8·9.

This inactive ketone has therefore the formula $C_7H_{12}O$, and proved to be 1-methyl*cyclo*hexan-3-one, since it yielded a sparingly soluble dibenzylidene derivative melting at 118°, and a phenylsemicarbazone melting at 186°. (Found, C=68·4; H=7·7. $C_{14}H_{19}$ requires C=68·5; H=7·8 per cent.)

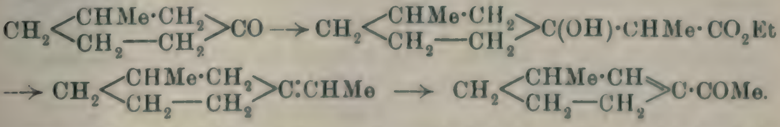
Since during the oxidation of *d*(3)-dihydrosylveterpineol, (+) and inactive 1-methyl*cyclo*hexan-3-one, acetone is also produced, identified by the iodoform reaction, it is clear that the tion can only be represented thus:



$$CH_2{<}\begin{smallmatrix}CHMe\cdot CH_2\\ CH_2{-}{-}CH_2\end{smallmatrix}{>}CH\cdot CMe_2\cdot OH \longrightarrow CH_2{<}\begin{smallmatrix}CHMe\cdot CH_2\\ CH_2{-}{-}CH_2\end{smallmatrix}{>}CO + COMe_2.$$

### *Synthesis of* d(1)-*Dihydrosylveterpineol.*

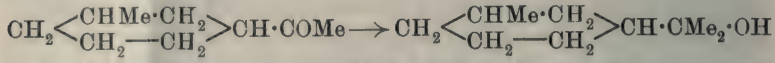
In carrying out this synthesis, *d*-1-methyl*cyclo*hexan-3-one (from pulegone) was converted by means of ethyl *α*-bromopropionate and zinc into 1-methyl-3-ethylidene*cyclo*hexane by a process which has already been described (*Annalen*, 1908, **360**, 51), and from this hydrocarbon the nitrosochloride and then the unsaturated ketone were prepared:



$$CH_2{<}\begin{smallmatrix}CHMe\cdot CH_2\\ CH_2{-}{-}CH_2\end{smallmatrix}{>}CO \rightarrow CH_2{<}\begin{smallmatrix}CHMe\cdot CH_2\\ CH_2{-}{-}CH_2\end{smallmatrix}{>}C(OH)\cdot CHMe\cdot CO_2Et \rightarrow CH_2{<}\begin{smallmatrix}CHMe\cdot CH_2\\ CH_2{-}{-}CH_2\end{smallmatrix}{>}C{:}CHMe \longrightarrow CH_2{<}\begin{smallmatrix}CHMe\cdot CH\\ CH_2{-}{-}CH_2\end{smallmatrix}{\gg}C\cdot COMe.$$

The *d*-3-methyl-$\Delta^1$-*cyclo*hexenyl methyl ketone thus obtained is readily converted by reduction with hydrogen in the presence of colloidal palladium into 3-methyl*cyclo*hexyl methyl ketone, which had already been prepared by Haworth and Wallach (*Annalen*, 1912, **389**, 193) by the reduction of the nitrosochloride mentioned above. The physical properties of this ketone were not determined at that time; they have now been found to be as follows: B. p. 199—202°; $d_{19}$ 0·912°; $n_D$ 1·4517 at 19°; M 41·39 (calc., 41·61).

The pure ketone was now converted into *d*(1)-dihydrosylveterpineol *d*(1)-*m*-menthanol(8):



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{matrix}>CH\cdot COMe \longrightarrow CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$$

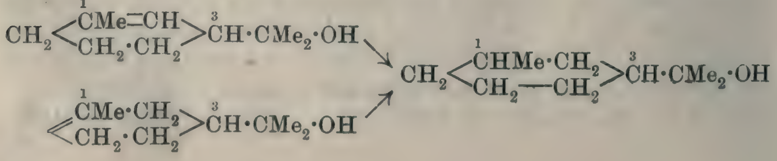
by the action of magnesium methyl iodide in the usual manner, and the tertiary alcohol thus obtained had not only the same odour as the specimen prepared by the reduction of *d*(3)-sylveterpineol (p. 1238), but also, with the exception of a somewhat lower rotation, the same physical constants:

0·1938 gave 0·5540 $CO_2$ and 0·2205 $H_2O$. C=76·6; H=12·7.

$C_{10}H_{20}O$ requires C=76·8; H=12·9 per cent.

B. p. 206—209°; $d_{20}$ 0·9100°; $n_D$ 1·4663 at 20°; $\alpha_D$ +1·96° (in methyl alcohol); M 47·50 (calc. 47·55). The two substances exhibit
slight difference in respect of the melting points of their phenyl-
anes, since the phenylurethane of dihydrosylveterpineol from
pineol melts at about 74°, whereas that of synthetical dihydro-
pineol, although it is in appearance and properties exactly
the substance of melting point 74°, melts at 82—83°.
difference could be explained it was important to prove
wo substances were actually structurally identical, and
was done by oxidation with chromic acid under the conditions given on p. 1238, when, like the dihydrosylveterpineol from sylveterpineol, the synthetical substance was converted into acetone and 1-methyl*cyclo*hexan-3-one, but with this difference, that, in the place of the inactive ketone obtained in the first case, the ketone resulting from the oxidation of synthetical dihydrosylveterpineol was the active modification, which has $\alpha_D$ +8·8° and yields a phenylsemicarbazone melting at 169° and a dibenzylidene derivative melting at 127°. It seems at first sight remarkable that, whilst the strongly active dihydrosylveterpineol from sylveterpineol ($\alpha_D$ +10·35°) yields, on oxidation, inactive 1-methyl*cyclo*hexan-3-one, the less active synthetical dihydrosylveterpineol ($\alpha_D$ +1·96°) should, under the same conditions, yield the active ketone, but a careful consideration of the question suggests not only an explanation for this difference, but at the same time supplies further confirmation of the constitutional formulæ proposed for sylveterpineol (p. 1237).

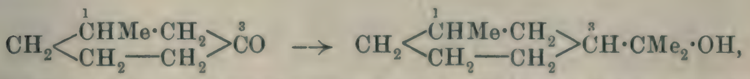
The two constituents of sylveterpineol contain one asymmetric carbon atom (3), which remains intact when this substance is reduced to dihydrosylveterpineol:



$$CH_2<\begin{matrix}\overset{1}{C}Me{=}CH\\ CH_2\cdot CH_2\end{matrix}>\overset{3}{C}H\cdot CMe_2\cdot OH \searrow \qquad CH_2<\begin{matrix}\overset{1}{C}HMe\cdot CH_2\\ CH_2—CH_2\end{matrix}>\overset{3}{C}H\cdot CMe_2\cdot OH \qquad \nearrow \leqslant\begin{matrix}\overset{1}{C}Me\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>\overset{3}{C}H\cdot CMe_2\cdot OH$$

Carbon atom (I) in the two formulæ for sylveterpineol is not an asymmetric one, and when it becomes asymmetric by the reduction to *d*(3)-dihydrosylveterpineol, it can have no effect on the rotation of this terpineol, unless, indeed, asymmetric synthesis is assumed to take place. It follows, therefore, that the activity of *d*(3)-dihydrosylveterpineol from sylveterpineol is conditioned only by carbon atom (3), and, as the asymmetry of this is destroyed when this terpineol is oxidised to 1-methyl*cyclo*hexan-3-one, the inactive ketone should result, and this is actually the case.

In synthesising *d*(1)-dihydrosylveterpineol from *d*-1-methyl*cyclo*hexan-3-one:



$$CH_2{<}\begin{matrix}\overset{1}{C}HMe\cdot CH_2\\ CH_2{-}CH_2\end{matrix}{>}\overset{3}{C}O \longrightarrow CH_2{<}\begin{matrix}\overset{1}{C}HMe\cdot CH_2\\ CH_2{-}CH_2\end{matrix}{>}\overset{3}{C}H\cdot CMe_2\cdot OH,$$

the sign of the asymmetric carbon atom (I) in the ketone remains unchanged, but, on the other hand, carbon atom (3), although asymmetric, has been produced in equal quantities of *d*-(+) and *l*-(−).*

It is clear that this modification of *d*-dihydrosylveterpineol must, on oxidation, give active *d*-methyl*cyclo*hexan-3-one, and this is again the case. It follows, therefore, that the two *d*-sylveterpineols—the one obtained from sylveterpineol by reduction and the other synthetically from *d*-methyl*cyclo*hexan-3-one—are isomeric substances, the isomerism being due to spatial differences in the nature of the asymmetrical carbon atoms (1) and (3). This explanation supplies an interesting and satisfactory reason for the slight differences observed in their optical and other properties, such as the melting points of the phenylurethanes.

THE UNIVERSITIES OF ST. ANDREWS, MANCHESTER, AND GÖTTINGEN.

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* More strictly speaking, when sylveterpineol is reduced, the carbon atom (1) becomes an asymmetric one and, employing the usual formal conceptions of the spatial configurations of unsaturated compounds, it is evident that addition of hydrogen may occur at either side of the double linking, and consequently the distribution of atoms and groups about the carbon atom (1) may assume either the configuration *d*- (+) or *l*- (−). Judging by the difficulty experienced by chemists in establishing clear cases of asymmetric synthesis, the probabilities are considerably in favour of the production of equal numbers of molecules of each kind. If this were so, then any process which destroys the asymmetry of the carbon atom (3), will result in the production of a compound approximately one-half the molecules of which will contain carbon atom (1) in the *d*- (+) form, and the other half in the *l*- (−) form, and since this is the only asymmetric atom which remains, the product will be a nearly in active mixture. Similar considerations apply to the second case.

# CXXX.—*Cantharene and Other Hydrocarbons Allied to the Terpenes.*

By WALTER NORMAN HAWORTH.

THE dihydroxylenes, of which cantharene is perhaps the most interesting member, have several times within recent years claimed the attention of chemists, and yet as a class these hydrocarbons have never been completely investigated and definitely characterised.

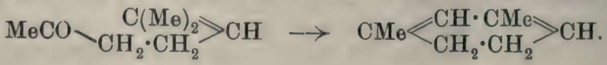
Cantharene itself was first prepared by Piccard in the course of his classical researches on cantharidine. It is a dihydro-*o*-xylene, $C_8H_{12}$, as it yields *o*-toluic and phthalic acids on oxidation, and its isolation as a degradation product of cantharic acid afforded a valuable clue to the structure of cantharidine. Further interest attaches to this hydrocarbon because its close resemblance in properties to the terpenes led Piccard to regard it as the first artificially prepared terpene (*Ber.*, 1878, **11**, 2122; 1892, **25**, 2453).

Notwithstanding the interesting character of this substance it does not appear to have ever been prepared sufficiently pure for spectrochemical examination, the only optical constant available being the refractive index of the crude oil containing *o*-xylene as impurity ($n_D = 1{\cdot}49118$; Harries and Antoni, *Annalen*, 1903, **328**, 115).

Later, Baeyer synthesised a dihydro-*p*-xylene (*Ber.*, 1892, **25**, 2122), which he regarded as 1 : 4-dimethyl-$\Delta^{1:4}$-*cyclo*hexadiene, since it was prepared from ethyl succinylsuccinate by methylation and subsequent hydrolysis, reduction, and dehydration. Unfortunately the physical constants of this substance were not determined, and are thus not available for comparison.

Auwers has recently described another dihydro-*p*-xylene isomeric with the above, namely, 1 : 4-dimethyl-$\Delta^{1:3}$-*cyclo*hexadiene (*Ber.*, 1908, **41**, 1816), which he characterised by physical methods and by oxidation to acetonylacetone.

A similar derivative of *m*-xylene figured for a long time in the literature as the product obtained by the elimination of water from methylheptenone by the use of various dehydrating reagents:



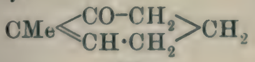
$$\mathrm{MeCO}\diagdown\begin{matrix}\mathrm{C(Me)_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!\!>\mathrm{CH} \longrightarrow \mathrm{CMe}\!<\!\begin{matrix}\mathrm{CH{\cdot}CMe}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!\!>\mathrm{CH}.$$

The hydrocarbon produced in this way has since been shown to consist principally of *m*-xylene and 1 : 3-dimethyl*cyclo*hexene, and to contain only little, if any, of the 1 : 3-dimethyl*cyclo*hexadiene (Wallach, *Annalen*, 1913, **395**, 74).

A dihydro-*m*-xylene is also mentioned by Harries and Antoni (*loc. cit.*), who prepared what they considered to be 1 : 3-dimethyl-$\Delta^{4:6}$-*cyclo*hexadiene by the dry distillation of the phosphate of 1 : 5-diamino-1 : 3-dimethyl*cyclo*hexane. The physical constants recorded for this hydrocarbon, however, seem clearly to indicate that it cannot have the arrangement of conjugated double linkings suggested by these authors, and the compound in all probability is 1 : 3-dimethyl-$\Delta^{1:4}$-*cyclo*hexadiene. The somewhat drastic treatment involved in the preparation of this substance has, indeed, been found in analogous cases to give rise to heterogeneous mixtures, and, owing to the wandering of substituent groups, the application of these conditions seems untrustworthy as a means of preparing a pure, homogeneous hydrocarbon (compare Crossley, T., 1909, **95**, 930).

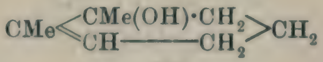
The close relationship which the dihydroxylenes bear to the members of the terpene group appeared to render them worthy of further investigation. With this object in view, a general method has been devised for the preparation of hydrocarbons of this character, the conditions employed being such as to lead to a homogeneous product of definitely known constitution.

When 1-methyl-$\Delta^{6}$-*cyclo*hexen-2-one (III) is treated with magnesium methyl iodide, the tertiary alcohol, 1 : 2-dimethyl-$\Delta^{6}$-*cyclo*hexen-2-ol or cantharenol (IV) is formed, which is a viscid liquid distilling at 167°, and is the terpineol of the cantharene series. The dehydration of this substance leads to the corresponding hydrocarbon, 1 : 2-dimethyl-$\Delta^{2:6}$-*cyclo*hexadiene (I), distilling at 135·5° (corr.):



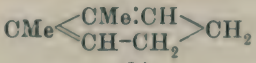
$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CO{-}CH_2}\\ \mathrm{CH{\cdot}CH_2}\end{matrix}{>}\mathrm{CH_2}$$

(III.)



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe(OH){\cdot}CH_2}\\ \mathrm{CH{-\!-\!-\!-}CH_2}\end{matrix}{>}\mathrm{CH_2}$$

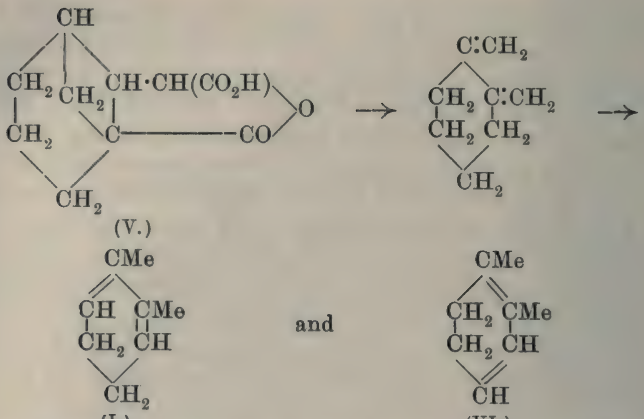
(IV.)



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CH{-}CH_2}\end{matrix}{>}\mathrm{CH_2}$$

(I.)

This dihydro-*o*-xylene seems to agree in all its properties with the hydrocarbon cantharene isolated by Piccard (*loc. cit.*); thus, it has a high refractive index which is comparable with the value found by Harries and Antoni (see p. 1242) for the hydrocarbon prepared from cantharidine, and it shows similar colour reactions and undergoes oxidation to *o*-toluic acid. The following scheme would seem to represent the change from cantharic acid (V) into cantharene, and although the latter substance would appear to consist principally of the compound I, yet it is extremely likely that there is some of the isomeric hydrocarbon (VI) also present:

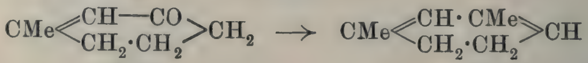


(V.)

(I.) and (VI.)

It is unfortunate that the additive halogen compounds of cantharene are not crystalline substances, and consequently no direct comparison of the derivatives of the hydrocarbon prepared from natural and synthetic sources is possible.

The second example of the conversion of a ketone into a dihydroxylene was 1-methyl-$\Delta^1$-*cyclo*hexen-3-one (VII), which reacts similarly with magnesium methyl iodide, but the reaction, resulting in the former case in the isolation of an alcohol, could not be arrested at this intermediate stage, the product isolated on the present occasion being the hydrocarbon 1 : 3-dimethyl-$\Delta^{1:3}$-*cyclo*hexadiene, distilling at 135° (corr.):



$$\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{-\!-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{CH_2} \longrightarrow \mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{\cdot}CMe}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{CH}$$

(VII.) (II.)

This substance possesses properties analogous to the terpene group of hydrocarbons, and is characterised by its readiness in absorbing oxygen and resinifying, so that the preparation of pure specimens of both this and the former hydrocarbon was only achieved by careful fractionation over sodium in the absence of air.

The physical constants of the three dihydroxylenes, the constitutional formulæ of which have been definitely established, are given below:

| | (I.) $\Delta^{1:5}$-Dihydro-*o*-xylene. | (II.) $\Delta^{1:3}$-Dihydro-*m*-xylene. | Auwers' $\Delta^{1:3}$-dihydro-*p*-xylene. |
|---|---|---|---|
| B. p. ......... | 135·5° | 135° | 135—138° |
| $D_4^{20}$ ........... | 0·8521 | 0·8373 | 0·830 |
| $n_D^{20}$ ..... ...... | 1·4895 | 1·4856 | 1·4797 |
| M ... .. ..... | 36·62 | 37·01 | 36·94 |

(M calculated, $C_8H_{12}|{=}^{2} = 36{\cdot}01$.)

The chief point of interest in this comparison is the uniformly high values for molecular refraction, M, which show in every case optical exaltation. This phenomenon is explicable on the grounds that all these hydrocarbons possess a conjugated system of double bonds. Whilst the boiling point remains almost identical in each case, yet the density and refractivity values increase according as the substituent methyl groups approach one another, that is, in the order, para to ortho. The three hydrocarbons studied form therefore a series in which the only variant is the position of the methyl groups, so that the influence of the proximity of such substituent groups on the molecular refraction can be evaluated. It will be noticed that the exaltation is less evident in the ortho- than in the case of the para-, whilst the meta-compound exhibits a still greater exaltation than either (compare Auwers and Eisenlohr, *J. pr. Chem.*, 1911, [ii], **84**, 37).

The physical constants recorded for the above hydrocarbons show a remarkably close parallelism with the values already found for the three xylenes themselves. The refractive indices tabulated below were determined by Sir W. H. Perkin (T., 1900, **77**, 267), and the densities quoted are those recently given by Richards in his Faraday Lecture (T., 1911, **99**, 1211):

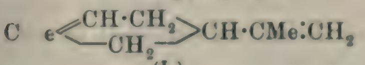
| | *o*-Xylene. | *m*-Xylene. | *p*-Xylene. |
|---|---|---|---|
| B. p. .......... | 144° | 139° | 136·2° |
| $D_4^{20}$............. | 0·8811 | 0·8658 | 0·8611 |
| $n_D$ ............ | 1·51136 | 1·50324 | 1·4991 |
| M ............ | 36·06 | 36·21 | 36·15 |

(M calculated, $C_8H_{10}|\overline{\phantom{x}}^3 = 35·54.$)

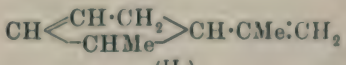
The same gradation in density and refractive power from the ortho- to the para-compound is noticeable, and there is a similar analogy between the two sets of values for molecular refraction.

This close comparison of the physical properties of the xylenes with their dihydro-derivatives lends support to the Kekulé formula representing these homologues of benzene, or preferably to Thiele's modification of this formula.

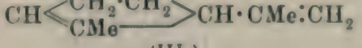
In this paper is also given an account of the synthesis of a new terpene of the *cyclo*pentane series, $C_9H_{14}$. Some time ago Haworth and Perkin (T., 1908, **93**, 573) published an investigation on the first known members of this series, consisting of three such hydrocarbons (I, II, III), and the present work contributes a fourth member of the group (IV):


$CH<\begin{matrix}CH\cdot CH_2\\CH_2\end{matrix}>CH\cdot CMe:CH_2$

(I.)

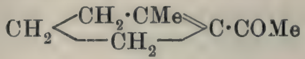

$CH<\begin{matrix}CH\cdot CH_2\\CHMe\end{matrix}>CH\cdot CMe:CH_2$

(II.)


$CH<\begin{matrix}CH_2\cdot CH_2\\CMe\end{matrix}>CH\cdot CMe:CH_2$

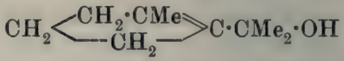
(III.)

The unsaturated ketone, 2-acetyl-1-methyl-Δ¹-*cyclo*pentene (V) has been characterised for the first time, and its semicarbazone (m. p. 221°) prepared. This ketone reacts with magnesium methyl iodide with formation of the terpineol (VI) of 1-methyl*iso*propenyl-*cyclo*pentene, which loses water and passes into the hydrocarbon (IV) distilling at 155—157°:



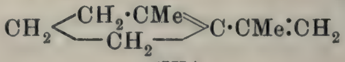
$$CH_2{<}\begin{matrix}CH_2\cdot CMe\\ CH_2\end{matrix}{>}C\cdot COMe$$

(V.)



$$CH_2{<}\begin{matrix}CH_2\cdot CMe\\ CH_2\end{matrix}{>}C\cdot CMe_2\cdot OH$$

(VI.)



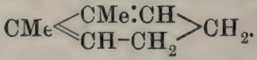
$$CH_2{<}\begin{matrix}CH_2\cdot CMe\\ CH_2\end{matrix}{>}C\cdot CMe{:}CH_2$$

(IV.)

The physical and chemical properties of these substances are given in the experimental part. It will be observed that the boiling point of the hydrocarbon (IV) is higher than that of any of the previous members of the series, and this is doubtless attributable to the system of conjugated double linkings which the compound possesses, a factor which is also responsible for the exaltation in the value for molecular refraction (see p. 1250).

## EXPERIMENTAL.

### *Synthesis of* 1 : 2-*Dimethyl*-Δ²﹕⁶-cyclo*hexadiene* (Δ¹﹕⁵-*dihydro-o-xylene*), $CMe{<}\begin{matrix}CMe{:}CH\\ CH{-}CH_2\end{matrix}{>}CH_2$.



When the nitrosochloride of 1-methyl-Δ¹-*cyclo*hexene * is digested with anhydrous sodium acetate in glacial acetic acid, hydrogen chloride is eliminated with the formation of the oxime of 1-methyl-Δ⁶-*cyclo*hexen-2-one. This unsaturated ketone is easily regenerated from the oxime by the agency of dilute mineral acid in the presence of formaldehyde, and serves as the starting point of the present synthesis (compare Wallach, *Annalen*, 1908, **359**, 302).

1-Methyl-Δ⁶-*cyclo*hexen-2-one reacts vigorously with an excess of magnesium methyl iodide in dry ether. The product, after keeping for several hours, was decomposed with ice and water, distilled in a current of steam, and the distillate extracted with ether, dried, and distilled. A colourless oil, boiling at 167° under ordinary pressure, passed over, and this appeared to lose water during the

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* The following physical constants of 1-methyl*cyclo*hexan-1-ol (m. p. 24°) were determined:

$$D_4^{20}=0{\cdot}9302\,;\ n_D=1{\cdot}4620\,;\ M=33{\cdot}70.\quad (\text{Calc. } M=33{\cdot}85.)$$

On digesting 1-methyl*cyclo*hexan-1-ol with 10 per cent. aqueous oxalic acid for three hours and submitting the product to distillation in steam, the corresponding hydrocarbon was formed, namely, 1-methyl-Δ¹-*cyclo*hexene, which, when rectified over sodium, distilled at 110—112°, and yielded a solid nitrosochloride melting at 95—97° (compare Wallach, *Annalen*, 1908, **359**, 287).

distillation. When the fractionation was carried out under diminished pressure, the pure carbinol, having the boiling point 132°/180 mm., was obtained. This substance, 1 : 2-dimethyl-$\Delta^6$-*cyclo*hexen-2-ol or cantharenol, has a faint odour of menthol, and with concentrated sulphuric acid gives a deep orange-red coloration, whilst with acetic anhydride and a drop of concentrated sulphuric acid it yields an intense violet solution, changing rapidly into blue:

0·1270 gave 0·3540 $CO_2$ and 0·1260 $H_2O$. C = 76·0; H = 11·0.

$C_8H_{14}O$ requires C = 76·2; H = 11·1 per cent.

The physical constants of this alcohol were determined:

$D_4^{20}$ 0·9528; $n_D = 1·4844$; M = 37·86 (Calc., M = 38·00).

In contact with phenylcarbimide, dehydration of the carbinol took place instantaneously with formation of diphenylcarbimide, so that the urethane could not be prepared.

The whole of the 1 : 2-dimethyl-$\Delta^6$-*cyclo*hexen-2-ol was converted into the hydrocarbon, 1 : 2-dimethyl-$\Delta^{2:6}$-*cyclo*hexadiene, by digestion with 8 per cent. aqueous oxalic acid. The product was distilled in a current of steam, extracted with ether, dried over potassium carbonate, and rectified over metallic sodium in an atmosphere of hydrogen. A colourless oil having a strong odour of turpentine, and distilling constantly at 135·5° (corr.), was collected:

0·0987 gave 0·3210 $CO_2$ and 0·0972 $H_2O$. C = 88·7; H = 11·0.

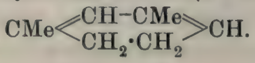
$C_8H_{12}$ requires C = 88·9; H = 11·1 per cent.

The hydrocarbon gave an orange-red coloration with concentrated sulphuric acid, and a carmine-red coloration, changing rapidly to reddish-brown, when to its solution in acetic anhydride a drop of concentrated sulphuric acid was added. It is further characterised by its extreme readiness in absorbing oxygen from the atmosphere and its tendency to polymerise to a hydrocarbon of higher boiling point; considerable difficulty was therefore encountered in the preparation of a specimen of such purity as to be available for analysis, and for the measurement of the physical constants of the substance:

$D_4^{20}$ 0·8521; $n_D = 1·4895$; M = 36·62 (Calc., M = 36·01).

The hydrocarbon was oxidised by digestion with dilute nitric acid (D 1·2), and after evaporation of the mineral acid in a vacuum a solid residue was obtained which yielded a pure specimen of *o*-toluic acid, melting at 103°.

### 1 : 3-*Dimethyl*-$\Delta^{1:3}$-cyclo*hexadiene* ($\Delta^{1:3}$-*Dihydro*-m-*xylene*),



$$\mathrm{CMe}\Big\langle\begin{matrix}\mathrm{CH{-}CMe}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big\rangle\mathrm{CH}.$$

When 1-methyl-$\Delta^1$-*cyclo*hexen-3-one, prepared according to Knoevenagel's method (*Annalen*, 1894, **281**, 94), was submitted to the Grignard reaction under the conditions described in the previous case (p. 1246), and using magnesium methyl iodide as before, a pleasant smelling, light, volatile oil was obtained, which was sparingly soluble in water. This was extracted, and the major portion distilled between 130° and 140° under the ordinary pressure, leaving a slight residue which possessed a phenolic odour. On refractionation over metallic sodium in an atmosphere of hydrogen, the fraction of low boiling point distilled constantly at 135—136°:

0·0928 gave 0·3027 $CO_2$ and 0·0918 $H_2O$. C = 88·9; H = 11·0.
$C_8H_{12}$ requires C = 88·9; H = 11·1 per cent.

An attempt was made to isolate the corresponding carbinol which would be the intermediate product formed in the above Grignard reaction. Dehydration seems, however, to be effected by contact with Grignard's reagent even in the cold, so that only the hydrocarbon could be isolated.

1 : 3-*Dimethyl*-$\Delta^{1:3}$-cyclo*hexadiene* is a colourless liquid, possessing a distinctive odour similar to that of pinene; it readily undergoes oxidation in the air, and resinifies. With concentrated sulphuric acid it gives an orange coloration, whilst acetic anhydride containing a drop of concentrated sulphuric acid produces a claret solution.

The following are the physical constants:

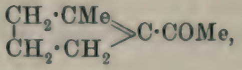
$D_4^{20}$ 0·8373; $n_D = 1·4856$; M = 37·01 (Calc., M = 36·01).

Klages (*Ber.*, 1907, **40**, 2362) mentions a substance identical in constitution with the above hydrocarbon, but the method of preparation, boiling point, and other important properties are not given.

The *Dibromide*.—A solution of bromine in chloroform was slowly dropped into a well-cooled mixture containing 0·851 gram of the above hydrocarbon in 5 c.c. of chloroform, the bromine being readily absorbed. After 1·26 grams of bromine had been added, corresponding with one molecule, hydrogen bromide began to be evolved, although the solution remained only pale yellow on keeping. On the further addition of bromine the halogen continued to be absorbed with displacement of hydrogen, until in all 2·16 grams of bromine had been added, when the colour remained permanently red. Only liquid bromides could be isolated.

The *nitrosochloride* was prepared, and this also is a liquid.

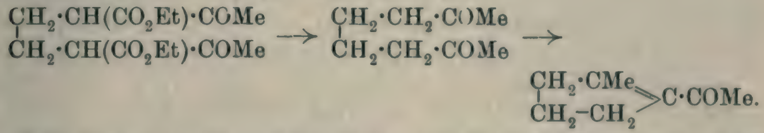
### 2-*Acetyl*-1-*methyl*-Δ¹-cyclo*pentene*,



$$\left.\begin{array}{l} CH_2\cdot CMe \\ CH_2\cdot CH_2 \end{array}\right> C\cdot COMe,$$

### *and its Semicarbazone.*

Marshall and Perkin first obtained this ketone by the hydrolysis of ethyl diacetyladipate with excess of methyl-alcoholic potassium hydroxide, diacetylbutane being an intermediate product which, under the conditions essential for the hydrolysis, undergoes internal condensation with loss of water and formation of the above unsaturated ketone (T., 1890, **57**, 242):



$$\begin{array}{l} CH_2\cdot CH(CO_2Et)\cdot COMe \\ CH_2\cdot CH(CO_2Et)\cdot COMe \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CH_2\cdot COMe \\ CH_2\cdot CH_2\cdot COMe \end{array} \longrightarrow \left.\begin{array}{l} CH_2\cdot CMe \\ CH_2-CH_2 \end{array}\right> C\cdot COMe.$$

The author has found the following to be the best method for the preparation of this ketone; crude ethyl diacetyladipate was digested for forty-eight hours with ten times its bulk of 10 per cent. aqueous sulphuric acid in a reflux apparatus, and then a brisk current of steam was passed through the liquid, when the unsaturated ketone was carried over. The steam distillate was saturated with ammonium sulphate, extracted twice with much ether, the extract dried over anhydrous magnesium sulphate, and the ether evaporated. The ketone distilled constantly at 189°, and the following physical constants were determined:

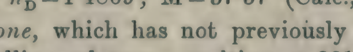
$$D_4^{20}\ 0{\cdot}9542;\ n_D = 1{\cdot}4869;\ M = 37{\cdot}37\ \ (\text{Calc., } M = 36{\cdot}49).$$

The *semicarbazone*, which has not previously been described, is a colourless, crystalline substance, melting at 221°, and is sparingly soluble in alcohol, from which it may be purified:

0·1086 gave 0·2372 $CO_2$ and 0·0812 $H_2O$. C = 59·5; H = 8·3.

$C_9H_{15}ON_3$ requires C = 59·7; H = 8·3 per cent.

### 1-*Methyl*-2-iso*propenyl*-Δ¹-cyclo*pentene*,



$$CH_2 \left< \begin{array}{l} CH_2\cdot CMe \\ CH_2 \text{———} \end{array} \right> C\cdot CMe{:}CH_2.$$

In order to prepare this hydrocarbon, a dry ethereal solution of 2-acetyl-1-methyl-Δ¹-*cyclo*pentene (20 grams) was carefully added to a Grignard reagent consisting of 48 grams of methyl iodide and 8·2 grams of magnesium. A violent reaction ensued, and the product was kept overnight, then decomposed with ice, and the ether was removed by distillation in a current of steam. An oil possessing a pungent odour collected in the receiver, and this was extracted with ether, the product being fractionated under diminished pressure. The first fraction distilled at 85—95°/

45 mm., and a small proportion at 95—130°/45 mm. The first fraction was carefully redistilled over metallic sodium at the ordinary pressure in an atmosphere of hydrogen, when it was found to boil at 155—157°:

0·1431 gave 0·4627 $CO_2$ and 0·1426 $H_2O$. C=88·2; H=11·1.

$C_9H_{14}$ requires C=88·6; H=11·4 per cent.

The physical properties of this pure specimen were determined:

$D_4^{20}$ 0·8515; $n_D$=1·4892; M=41·36 (Calc., M=40·63).

1-*Methyl*-2-iso*propenyl*-$\Delta^1$-cyclo*pentene* is a terpene of the methyl*iso*propyl*cyclo*pentane series (compare Haworth and Perkin, T., **93**, 573); it possesses an odour similar to that of dipentene, and exhibits a tendency to polymerise to hydrocarbon which distil at a temperature intermediate between 157° and 175°. It is very unstable in contact with the air, from which it readily absorbs oxygen and resinifies. With acetic anhydride and a drop of concentrated sulphuric acid, it gives a deep crimson coloration exactly as do the members of the terpene group.

The second fraction, boiling at 95—130°/45 mm., was refractionated, when it was found to distil at 115°/30 mm., accompanied by the loss of a little water, and consequently good analytical results could not be obtained. There can be no doubt, however, that the substance distilling at the above temperature was the terpineol, 1-methyl-2-*iso*propenol-$\Delta^1$-*cyclo*pentene, since the above hydrocarbon was obtained from it by the elimination of water. It possesses a pleasant odour resembling that of camphor.

The *dibromide*.—0·892 Gram of 1-methyl-2-*iso*propenyl-$\Delta^1$-*cyclo*pentene was dissolved in 5 c.c. of chloroform, and the solution cooled to −10°. A solution of bromine in chloroform was gradually added from a burette, and after the first few drops the product assumed a deep red colour, although bromine continued to be absorbed. When 1·164 grams of bromine had been added, hydrogen bromide began to be evolved in copious clouds on each subsequent addition of the bromine solution. The end point of absorption was thus easy of detection. This amount of bromine is equivalent to one molecule, 1·17 grams being the theoretical amount required for the weight of hydrocarbon taken. The solution, which had acquired a deep permanganate coloration, was allowed to evaporate in the air, when a heavy oil remained, which did not crystallise.

The author is indebted to the Chemical Society for a grant, which has defrayed the expenses of this investigation.

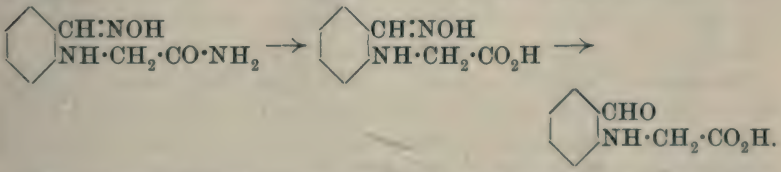
United College of St. Salvator and St. Leonard,
University of St. Andrews.

# CXXXI.—*The Synthesis of* o-*Aldehydophenylglycine.*

### By Wilhelm Gluud.

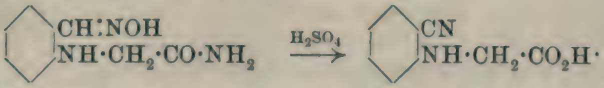
In spite of the importance of phenylglycine-*o*-carboxylic acid in technical chemistry, the corresponding *o*-aldehydophenylglycine does not seem to have been prepared. The synthesis of this compound was a matter of considerable interest, as it seemed likely it might be an excellent source for the preparation of indole and its derivatives.

The direct interaction of *o*-aminobenzaldehyde and chloroacetic acid or its ester did not give good results, still less if the oxime was used instead of the aldehyde. A much better method was found in the decomposition of the oxime with chloroacetamide in the presence of calcium carbonate. The oxime of *o*-aldehydophenylglycineamide thus obtained, on boiling with alkali, gave the oxime of *o*-aldehydophenylglycine. By careful treatment of the oxime of *o*-aldehydophenylglycineamide with dilute sulphuric acid, the oximo-group also was eliminated, and *o*-aldehydophenylglycine obtained.



The *o*-aminobenzaldoxime required was prepared from *o*-nitrobenzaldehyde by reducing the oxime with ammonium sulphide according to the method given by Gabriel and Meyer (*Ber.*, 1881, **14**, 2339; compare also Gabriel, *Ber.*, 1903, **36**, 803).

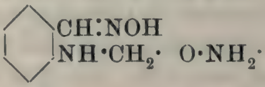
When the oxime of *o*-aldehydophenylglycineamide was treated with concentrated sulphuric acid, a good yield was obtained of a crystalline compound, which, from its melting point and other properties, I believe to be *o*-cyanophenylglycine:



When the amide or the corresponding oxime of *o*-aldehydophenylglycine was fused with potassium hydroxide, phenylglycinecarboxylic acid and indigotin were obtained in quantities varying with the experimental conditions. The formation of indigotin was ascribed to the intermediate production of *o*-cyanophenylglycine. On dry distillation with lime, both the amide-aldoxime and the aldehyde gave indole or its derivatives. This reaction and other experiments with *o*-aldehydophenylglycine will be further investigated.

## EXPERIMENTAL.

### *Oxime of* o-*Aldehydophenylglycineamide,*



*o*-Aminobenzaldoxime (22·5 grams) was heated with 17 grams of chloroacetamide, 9 grams of calcium carbonate, and 350 c.c. of water for three hours under a reflux condenser. The mixture was allowed to cool, and the crystalline powder formed was collected, treated with a small quantity of cold concentrated hydrochloric acid, and again collected, washed, and dried on a water-bath. The yield was 25·5 grams, or 80 per cent. of the theoretical. This compound was pure enough for most purposes, but for analysis 1 gram was redissolved in 200 c.c. of boiling water, from which the *oxime* crystallised in small, microscopic, colourless prisms or octahedra, melting and decomposing at 212—214:

0·1549 gave 0·3186 $CO_2$ and 0·0808 $H_2O$. C=56·10; H=5·84.
0·1437 „ 26 c.c. $N_2$ at 15° and 764 mm. N=21·33.
$C_9H_{11}O_2N_3$ requires C=55·93; H=5·74; N=21·76 per cent.

The oxime is scarcely soluble in cold water, and very sparingly so in organic media; when warmed with alkali it gives off ammonia. When heated with lime, considerable quantities of oily distillates are obtained, which give a marked reaction with pine-shavings, the odour of indole being at the same time observed.

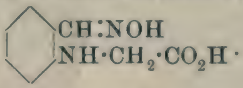
The oxime was fused with potassium hydroxide, the reaction being carried out as follows. 7·5 Grams of potassium hydroxide and 2 c.c. of water were heated to 170°, and 0·6 gram of the oxime added to the fused mass. When it was well mixed, it was left in a closed vessel, with a stream of hydrogen passing through it, for two hours at 210—220°. The fused mass was treated with water, and the mixture, which had a dark colour owing to the formation of indigotin, was extracted with ether. The colouring-matter collected at the top, so that the aqueous lower layer could be separated. The latter was acidified with concentrated hydrochloric acid, and then extracted three times with ether, the ethereal solution evaporated, and the residue crystallised from water. In this way 0·2 gram of phenylglycine-*o*-carboxylic acid was obtained. Any rise in temperature was found to produce a corresponding increase in the yield of indigotin.

### o-*Cyanophenylglycine.*

The oxime described above (0·5 gram) was warmed with 5 c.c. of concentrated sulphuric acid until it was dissolved. The solution was then poured on ice, when microscopic needles soon separated, which were collected, washed, and dried on a water-bath (0·4 gram). The compound melted and decomposed at about 192° after a previous short sintering.

It is scarcely soluble in alcohol or other organic solvents, but readily so in warm water, from which it does not crystallise. The substance is in all probability *o*-cyanophenylglycine, identical with that prepared according to the method described in D.R.-P. 206903 (*Chem. Zentr.*, 1909, i, 807). Analysis gave nearly theoretical figures, but this cannot be entirely depended on, as the substance could not be purified by recrystallisation.

### *Oxime of* o-*Aldehydophenylglycine*,

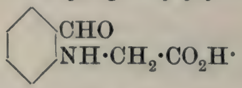


In order to prepare this compound, 10 grams of the oxime of *o*-aldehydophenylglycineamide were boiled with 125 c.c. of 2*N*-sodium hydroxide until all odour of ammonia had disappeared. The mixture was then cooled and treated with 250 c.c. of *N*-sulphuric acid. The crystals separating were collected and recrystallised from 125 c.c. of water. After drying on a water-bath, the yield of the *oxime* of o-*aldehydophenylglycine* was 8·2 grams, or 82 per cent. of the theoretical. The compound forms compact, spicular crystals, which melt and evolve gas at 134°. They are exceedingly soluble in ether, acetone, or alcohol, and fairly so in hot water or chloroform. For analysis, the compound was again recrystallised from water, then dissolved in methyl alcohol, and precipitated with water.

The product was almost pure white, with a yellow tinge. It was dried for an hour over phosphoric acid at 100°/10—12 mm., and then analysed:

0·2139 gave 0·1013 $H_2O$ and 0·4386 $CO_2$. C = 55·92; H = 5·30.
0·1193 „ 14·8 c.c. $N_2$ at 20° and 758 mm. N = 14·21.
$C_9H_{10}O_3N_2$ requires C = 55·64; H = 5·19; N = 14·44 per cent.

### o-*Aldehydophenylglycine*,



The oxime of *o*-aldehydophenylglycineamide (3 grams) was boiled with 150 c.c. of 5*N*-sulphuric acid under a reflux condenser for ten minutes, then cooled, and the solution extracted twice with about 50 c.c. of ether. The ether was evaporated, and the residue dissolved in 50 c.c. of boiling xylene. On cooling, o-*aldehydophenylglycine* crystallised in aggregates of compact plates or tablets (1 gram). It is readily soluble in warm water, ethyl alcohol, or amyl alcohol, but sparingly so in benzene or chloroform.

On heating alone, or better with lime, a strong odour of indole is observed, and the vapours give a marked reaction with pine-shavings.

If the hot aqueous solution is mixed with a solution of phenylhydrazine in glacial acetic acid, a voluminous precipitate is formed, consisting of fine, microscopic needles, which are only very sparingly soluble in hot water. The aldehyde also shows distinctly the colour reaction with acid magenta.

The aldehyde was purified by recrystallisation, first from methyl alcohol, and afterwards from a mixture of equal parts of water and methyl alcohol. The product, after drying in a desiccator over phosphoric acid, is colourless and without odour, and melts at 176—177° to a red liquid, from which a slow evolution of gas takes place:

0·2919 gave 0·6458 $CO_2$ and 0·1358 $H_2O$. C = 60·34; H = 5·21.
0·1086 „ 7·5 c.c. $N_2$ at 18° and 758 mm. N = 7·98.

$C_9H_9O_3N$ requires C = 60·31; H = 5·06; N = 7·82 per cent.

When fused with potassium hydroxide, the aldehyde yields either phenylglycine-*o*-carboxylic acid or indigotin, according to the conditions. The calcium salt of *o*-aldehydophenylglycine is easily obtained by dissolving the aldehyde in *N*-sodium hydroxide and adding calcium chloride solution, when the calcium salt crystallises out. It seems to be a very suitable material for the preparation of indole or its derivatives.

Davy Faraday Laboratory.

# CXXXII.—*The Purification of Acetone by means of Sodium Iodide.*

By KATHLEEN SHIPSEY and EMIL ALPHONSE WERNER.

IN a recent note (P., 1913, **29**, 117) it was shown that sodium iodide is capable of uniting with acetone to form a well defined crystalline compound having the composition $NaI,3C_3H_6O$, which easily gives off all the acetone on gentle warming. The compound may be readily prepared by dissolving anhydrous sodium iodide to the point of saturation in hot acetone and allowing the solution to cool to the ordinary temperature; if the liquid is cooled to about −8° by means of ice and salt, the yield of crystals is largely increased.

Experiments have been made with the object of testing if the production of the above compound could be used for the preparation of pure acetone from the commercial material; the results, as seen below, are very satisfactory. A sample of ordinary dry acetone (about 500 c.c.) was distilled from a round-bottomed flask, provided with a three-section Young's evaporator still-head, and gave the following results: (*a*) b. p. corrected to 760 mm. = 55·9—56·3°; (*b*) $D^{0°}_{4°}$ 0·8152; (*c*) a few c.c. when added to a dilute solution of potassium permanganate caused immediate reduction of the latter. A quantity of the compound $NaI,3C_3H_6O$ was prepared by dissolving 100 grams of anhydrous sodium iodide in the fresh distillate by heating gently on the water-bath; the crystals which separated on cooling were drained off so far as possible from the mother liquor, and quickly transferred to a dry flask, attached to a suitable condenser and receiver, and the acetone rapidly distilled off by gentle heat. The distillate after remaining for twenty-four hours over anhydrous calcium chloride was redistilled, using an evaporator still-head as before; the following results were obtained: (*a*) b. p. at 760 mm. 56·1—56·2°; (*b*) $D^{0}$ = 0·8130; (*c*) a few c.c. added to solution of potassium permanganate produced no change even after standing for fifteen minutes.

A specimen of pure acetone from "bisulphite" (Kahlbaum) dried over calcium chloride gave (*a*) b. p. at 760 mm. 56·1—56·2°; (*b*) $D^{0°}_{4°}$ = 0·8138; (*c*) no reducing action on potassium permanganate.

Timmermans, in the course of a careful investigation, "Recherches expérimentales sur la densité des liquides en dessous de 0°" (*Sci. Proc. Roy. Dubl. Soc.*, 1912, **13**, 330), has determined the boiling points and densities of specimens of acetone from bisulphite, purified by redistillation from several different dehydrating agents; the purest product obtained by distillation from phosphoric oxide gave the values: (*a*) b. p.$=56{\cdot}10^\circ \pm 1$; (*b*) $D^0_4 = 0{\cdot}81249 \pm 3$, whilst a specimen from bisulphite (Kahlbaum) redistilled from calcium chloride gave this investigator the constants: b. p. 56·1° and $D^0_4 = 0{\cdot}8137$, a result almost identical with that found by us for a specimen purified in a similar manner. It is thus seen from the results just recorded that it is possible by means of sodium iodide to obtain pure acetone from the commercial article in a very simple manner, and whilst the product is quite equal in purity to that obtainable by the rather laborious bisulphite method, it is obvious that the process has the great advantage of being workable in a continuous manner, since the sodium iodide obtained after distilling off the acetone from the crystalline compound can be used repeatedly for obtaining a further supply of the compound either from the mother liquor or from a fresh quantity of ordinary acetone. In connexion with this point it was noticed that the sodium iodide left after distillation of the acetone from the crystals $NaI,3C_3H_6O$ was much more readily soluble in fresh acetone than the original salt used; this was found to be due to the abstraction of a certain amount of water from the acetone by the anhydrous salt, with formation of some of the dihydrate. The latter salt may be easily dissolved in its own weight of acetone at the ordinary temperature, and the resulting solution when cooled to about −8° yields a considerable quantity of the acetone compound, for this reason: the hydrated sodium iodide can be used with advantage for the preparation of a quantity of pure acetone when there is no desire to go beyond the trouble of a single operation.

The following results represent the wide difference in the proportions of pure acetone obtained in a single operation, using the different specimens of sodium iodide:

| | Calculated on weight of crude acetone used. |
|---|---|
| I. Fresh anhydrous sodium iodide, yield........ ...... | 26·8 per cent. |
| II. Sodium iodide left after distilling the acetone from the compound $NaI,3C_3H_6O$ ......... | 48·1 ,, ,, |
| III. $NaI,2H_2O$ ............................................ | 70·0 ,, ,, |

So far as could be ascertained, the purity of the acetone was the same in each case. It may be mentioned in conclusion that whereas the compound $NaHSO_3,C_3H_6O$ contains only 35·8 per cent. of acetone, the compound $NaI,3C_3H_6O$ can yield without loss 53·7 per cent. of the ketone, and this yield is exceeded from the crystalline deposit obtained by cooling the acetone solution in a mixture of ice and common salt, indicating the formation of a compound containing a still larger proportion of acetone of crystallisation.

## EXPERIMENTAL.

The following experimental details explain the results recorded above:

I. One hundred grams of finely powdered anhydrous sodium iodide required for complete solution 440 grams of ordinary acetone at the boiling point.

The solution was cooled in a mixture of ice and salt to $-8^\circ$.

Weight of crystals obtained = 198 grams.

Weight of pure acetone on distillation = 118 grams.

Weight of residual sodium iodide = 70 grams.

There was a loss of 10 grams of acetone; this is partly due to vaporisation from the crystals during the process of draining away the mother liquor.

II. One hundred grams of sodium iodide obtained from a previous distillation of the compound $NaI,3C_3H_6O$ required for complete solution 270 grams of acetone at the boiling point. Solution cooled as before.

Weight of crystals obtained = 210 grams.

Weight of pure acetone on distillation = 130 grams.

Weight of residual sodium iodide = 78 grams.

III. One hundred grams of $NaI,2H_2O$ taken, dissolved in 100 grams of acetone at the ordinary temperature. Cooled as before.

Weight of crystals obtained = 138 grams.

Weight of pure acetone on distillation = 70 grams.

Weight of residual sodium iodide = 62 grams.

The theoretical yield of acetone from 138 grams of the compound $NaI,3C_3H_6O$ is 74·1 grams; the result which is in close agreement with this indicates that this compound only separates even at the low temperature when the hydrated sodium iodide is used; the presence of a relatively large proportion of water probably prevents the formation of a compound containing a larger proportion of acetone. It should be noted that the above proportions do not represent a saturated solution of sodium iodide dihydrate in the acetone, as in I and II; from a stronger solution it would not be possible easily to drain off the crystals so as to obtain pure acetone from the product.

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# CXXXIII.—*Colour and Constitution of Azomethine Compounds. Part III.*

By FRANK GEORGE POPE and WINIFRED ISABEL WILLETT.

ONE of the authors, in conjunction with R. Fleming (T., 1908, **93**, 1918), pointed out that the salts of the azomethine compounds and their ethers exhibited an absorption totally different from that shown by the azomethines themselves, and suggested that the explanation of this fact was due to such substances existing as oxonium salts, whilst the azomethines possessed a normal configuration. A similar condition was also shown by Pope (*ibid.*, 533) to exist in the case of azomethine compounds containing a nitro- and a hydroxyl group in the para-position in each nucleus, the alkali salts showing an absorption markedly different from that exhibited by the azomethines, and the conclusion was drawn that in alkaline solution the compounds in question possessed a quinonoid configuration.

These results agree with Hewitt and Mitchell's observation (T. 1907, **91**, 1251) that the lengthening of the chain of alternate double and single linkings accompanies the shifting of the absorption to the red end of the spectrum. In the hope of further confirmation of this fact, we have endeavoured to increase the length of the chain by preparing azomethine compounds from aminoazobenzene and *p*-nitroaminoazobenzene, but unfortunately in the latter case, although various methods of condensation have been tried, we have not been able to obtain any azomethines from the nitroaminoazobenzene.

Several azomethines prepared from aminoazobenzene have been obtained, and are described below, whilst one or two compounds related to *p*-nitroaminoazobenzene are also characterised.

## EXPERIMENTAL.

Benzylideneaminoazobenzene has been obtained by Berju (*Ber.*, 1884, **17**, 1403), who gives the melting point as 128°, but we find that the corrected value is 130·5° (Found, C = 79·99; H = 5·28; N = 14·51. Calc., C = 80·00; H = 5·26; N = 14·74 per cent.).

p-*Hydroxybenzylideneaminoazobenzene*,

$$HO\cdot C_6H_4\cdot CH:N\cdot C_6H_4\cdot N_2\cdot C_6H_5,$$

was prepared by mixing equivalent quantities of its generators in hot alcoholic solution. The crystalline precipitate obtained is collected, washed, dried, and recrystallised from boiling toluene, separating from the solvent in small, orange-yellow needles, which melt at 231° (uncorr.):

0·1436 gave 0·400 $CO_2$ and 0·0622 $H_2O$. C=75·96; H=5·13.
0·085 „ 10·4 c.c. $N_2$ at 21° and 750 mm. N=14·02.
$C_{19}H_{15}ON_3$ requires C=75·75; H=4·98; N=13·95 per cent.

p-*Methoxybenzylideneaminoazobenzene*,

$$MeO{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_5,$$

was obtained similarly from anisaldehyde and aminoazobenzene. It crystallises from glacial acetic acid in orange-brown plates, which melt at 149°:

0·1592 gave 0·4433 $CO_2$ and 0·0789 $H_2O$. C=76·0; H=5·51.
$C_{20}H_{17}ON_3$ requires C=76·19; H=5·4 per cent.

p-*Nitrobenzylideneaminoazobenzene*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_5,$$

obtained similarly from *p*-nitrobenzaldehyde and aminoazobenzene, on recrystallisation from glacial acetic acid separates in small, orange plates, which melt at 182·2° (corr.):

0·1128 gave 0·2836 $CO_2$ and 0·0434 $H_2O$. C=68·62; H=4·27.
$C_{19}H_{14}O_2N_4$ requires C=69·09; H=4·24 per cent.

2 : 4-*Dihydroxybenzylideneaminoazobenzene*,

$$C_6H_3(HO)_2{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_5,$$

is obtained in the same manner from β-resorcylaldehyde and aminoazobenzene. It crystallises from alcohol in bronze leaflets, which melt and decompose at 163°:

0·1383 gave 0·3647 $CO_2$ and 0·0637 $H_2O$. C=71·92; H=5·12.
0·09 „ 10·4 c.c. $N_2$ (dry) at 19° and 741·4 mm. N=13·17.
$C_{19}H_{15}O_2N_3$ requires C=71·94; H=4·73; N=13·25 per cent.

With regard to the absorption spectra of the above compounds, the curves show a great similarity to that given by aminoazobenzene (Hewitt and Thomas, T., 1909, **95**, 1295), the positions of the heads of the bands being as follows:

| | | | |
|---|---|---|---|
| $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$ | about | 1/λ | 2600 |
| $C_6H_5{\cdot}N_2{\cdot}C_6H_4N{:}CH{\cdot}C_6H_4$ | „ | 1/λ | 2610 |
| $C_6H_5{\cdot}N_2{\cdot}C_6H_4N{:}CH{\cdot}C_6H_4{\cdot}NO_2$ | „ | 1/λ | 2610 |
| $C_6H_5{\cdot}N_2{\cdot}C_6H_4N{:}CH{\cdot}C_6H_4{\cdot}OH$ | „ | 1/λ | 2670 |
| $C_6H_5{\cdot}N_2{\cdot}C_6H_4N{:}CH{\cdot}C_6H_4{\cdot}OMe$ | „ | 1/λ | 2670 |

The *p*-nitroaminoazobenzene used was prepared by the method of the Aktien-Gesellschaft für Anilinfabrikation (D.R.-P. 131860), in which process diazotised *p*-nitroaniline is coupled with the sodium salt of monomethylaniline-ω-sulphonic acid, and the resulting compound decomposed with a warm dilute solution of sodium hydroxide.

The sodium salt of methylaniline-ω-sulphonic acid,

$$C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}SO_3Na,H_2O,$$

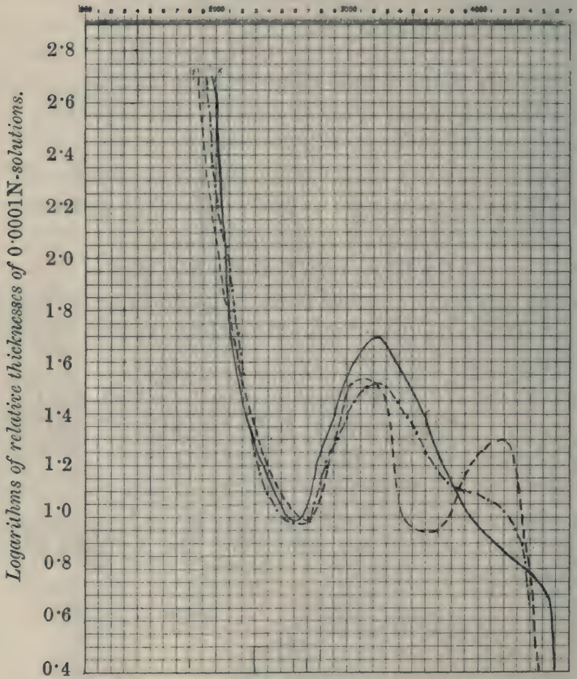
prepared by the condensation of aniline, formaldehyde, and sodium hydrogen sulphite, crystallises from dilute alcohol in small, colourless needles, which are very soluble in water:

0·1622 gave 9·7 c.c. $N_2$ (dry) at 16° and 740 mm. N = 6·88.
0·3818 „ 0·1217 $Na_2SO_4$. Na = 10·32.
0·1705 lost 0·0139 at 110°. $H_2O = 8·15$.

$C_7H_8O_3NSNa,H_2O$ requires N = 6·7; Na = 10·13; $H_2O$ = 7·93 per cent.

FIG. 1.

*Scale of oscillation frequencies.*



——— curve: $C_6H_5·N_2·C_6H_4·N:CH·C_6H_5$.
– – – – „ $C_6H_5·N_2·C_6H_4·N:CH·C_6H_4·OMe$.
–·–·– „ $C_6H_5·N_2·C_6H_4·N:CH·C_6H_4·NO_2$.

In coupling diazotised *p*-nitroaniline with the above sodium salt, a red precipitate of the salt $NO_2·C_6H_4·N_2·C_6H_4·NH·CH_2·SO_3Na$ is obtained, and may be purified by crystallisation from a mixture of equal volumes of alcohol and water, separating from the solvent in small, red needles:

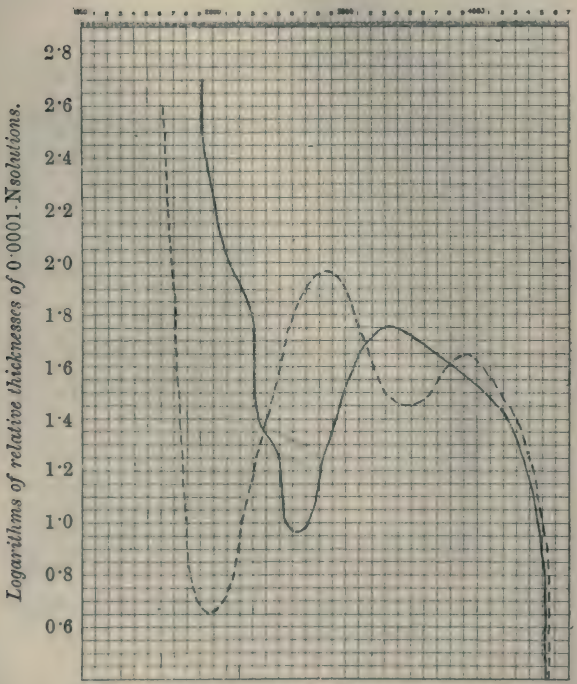
0·1524 gave 20 c.c. $N_2$ (dry) at 17° and 761 mm. N=15·47.

$C_{13}H_{11}O_5N_4SNa$ requires N=15·64 per cent.

At the request of Dr. J. T. Hewitt we have prepared a specimen of *p*-nitrobenzeneazobenzeneazophenol by diazotising *p*-nitroaminoazobenzene and coupling with an alkaline solution of phenol. On mixing the diazo-solution with the alkaline phenol solution, a chocolate-coloured precipitate is obtained; this was collected, washed, and recrystallised from glacial acetic acid, in which solvent it is sparingly soluble. It melts at 263°, and dissolves in concentrated sulphuric acid with a characteristic violet colour:

FIG. 2.

*Scale of oscillation frequencies.*



——— curve : p-*Nitrobenzeneazophenol in alcohol.*

- - - - ,, *Sodium salt.*

0·1198 gave 0·2753 $CO_2$ and 0·0397 $H_2O$. S=62·67; H=3·68.

0·1116 ,, 0·253 $CO_2$ ,, 0·036 $H_2O$. C=61·83; H=3·58.

0·1074 ,, 19·6 c.c. $N_2$ (dry) at 21° and 746 mm. N=20·78.

$C_{18}H_{13}O_3N_5$ requires C=62·24; H=3·74; N=20·18 per cent.

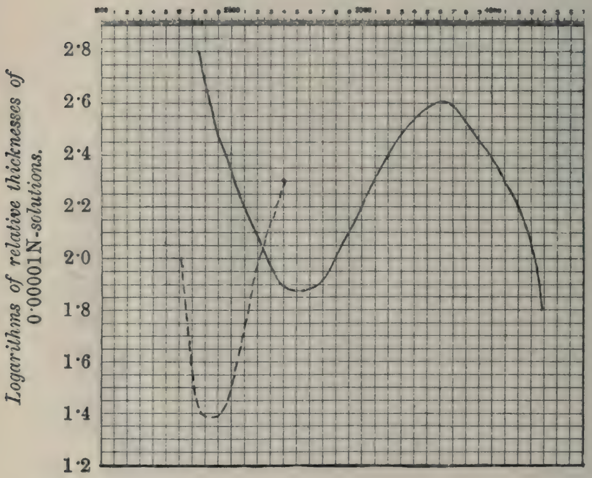
The hydrochloride, obtained by passing hydrogen chloride into a solution of the azophenol in xylene, is precipitated in small, violet needles.

The absorption curves of *p*-nitrobenzeneazophenol and *p*-nitrobenzeneazobenzeneazophenol and their sodium salts are shown in the annexed figures.

It will be noted that in the case of *p*-nitrobenzeneazophenol, the head of the band occurs at about 1/λ 2600, whilst on the addition of a little alkali, the head of the band is shifted to 1/λ 1950. With *p*-nitrobenzeneazobenzeneazophenol, the heads of the bands appear at 1/λ 2550 and 1/λ 1830, a fact agreeing with Hewitt and Mitchell's observation (T., 1907, **91**, 1251) that the longer the chain of alternate double and single linkings existing in the molecule, the less will be the chief oscillation frequency, and consequently the more blue the shade of the compound in question. This observation is strikingly confirmed in the case of the sodium salts of the two azo-compounds mentioned, for on dissolving them in dry xylene and adding an alcoholic solution of sodium ethoxide, *p*-nitrobenzeneazophenol gives a reddish-brown, crystalline precipitate of its sodium salt, whilst *p*-nitrobenzeneazobenzeneazophenol gives a purple, crystalline precipitate of the sodium salt.

Fig. 3.

*Scale of oscillation frequencies.*



——— curve : p-*Nitrobenzeneazobenzeneazophenol in alcohol.*
- - - - ,, *Sodium salt.*

In conclusion, we wish to tender our thanks to the Research Fund Committee of the East London College for a grant which has defrayed the cost of this investigation.

East London College,
University of London.

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# CXXXIV.—*The Absorption Spectra of Some Thio-derivatives of Benzene.*

By John Jacob Fox and Frank George Pope.

Phenyl mercaptan differs from phenol in several important particulars. Some of the salts of phenyl mercaptan, such as the lead, copper, and silver salts, are coloured; and phenyl mercaptan does not readily combine with diazonium compounds to give thiolazo-derivatives (Hantzsch and Freese, *Ber.*, 1895, **28**, 3241), but yields instead thiophenyl ethers. As is well known, phenyl mercaptan undergoes oxidation with great readiness, forming diphenyl disulphide.

In view of these differences from phenol, we have examined the spectra of phenyl mercaptan and other thio-derivatives of benzene to ascertain in what way the characteristic spectrum of benzene was altered by the introduction of the thio-groups. A few observations of this character were made by Purvis, Jones and Tasker (T., 1910, **97**, 2287).

The absorption spectrum of phenyl mercaptan exhibits no bands, but strong extensions of the spectrum occur in two places, one of which begins at about $1/\lambda$ 3600 (see diagram). This is in approximately the same position as the single persistent band of phenol (Hartley and Dobbie, T., 1902, **81**, 930; Baly and Ewbank, T., 1905, **15**, 1347). The addition of sodium ethoxide to a solution of phenyl mercaptan produces a profound change in the character of the spectrum. A band appears having its head at $1/\lambda$ 3730, and the whole spectrum is altered. The position of the bands in the case of sodium phenoxide and of sodium thiophenoxide is different, although in both the addition of sodium hydroxide has resulted in the displacement of the whole spectrum of the original substance towards the less refrangible region of the spectrum. This displacement of the spectrum appears to be a general effect of salt formation in phenols, and as regards the simpler phenols at all events the activity of the hydrogen atom of the hydroxyl or thiol group does not appear to have much to do with the displacement of the region of absorption (compare Baly and Ewbank, *loc. cit.*). When the displacement of the band consequent on salt formation is sufficiently great, the region of absorption cuts into the visible spectrum, and coloured salts result.

The absorption spectrum of diphenyl disulphide, $(C_6H_5\cdot S)_2$, has no bands, and is unaltered by the addition of sodium ethoxide.

Since the spectra of phenol and phenyl mercaptan were found to be entirely different from one another, it became of interest to ascertain whether similar differences would be shown by related compounds, such as diphenyl ether, $(C_6H_5)_2O$, and diphenyl sulphide, $(C_6H_5)_2S$. The spectrum of a chloroform solution of diphenyl ether has been shown by Purvis and McCleland (T., 1912, **101**, 1517) to contain two bands, and we found a similar spectrum with the alcoholic solution.

The spectrum of diphenyl sulphide differs entirely from that of diphenyl ether; it contains no bands, but there are two extensions of the spectrum as with phenyl mercaptan.

The examination of the spectra of the foregoing showed that the substitution of sulphur for oxygen had resulted in the suppression of the phenol bands except in the case of the sodium salt of phenyl mercaptan, and even in this case the spectrum was altered considerably (compare Purvis, Jones and Tasker, *loc. cit.*).

The spectra of the vapours of phenol, diphenyl ether, phenyl mercaptan, and diphenyl sulphide were also examined, and it was found that whilst the spectrum of phenol vapour showed a large number of sharp bands, that of phenyl mercaptan vapour showed only two very feeble diffuse bands. Diphenyl ether vapour, on the other hand, showed two bands in almost the same position as the bands in the solutions, whilst the spectrum of diphenyl sulphide contained a number of sharp, narrow bands.

The vapour spectrum of phenol vapour is striking. In the neighbourhood of the melting point of phenol, more than seventy narrow, sharp bands could be counted between λ 2800 and λ 2500, and only a few were found outside this region.* The largest number of bands was observed between 36° and 50·5°, and the following list shows the position of some of the principal bands at 44° and 765 mm. of pressure. The abbreviations are, as far as possible, those used by Purvis in his papers on vapour spectra

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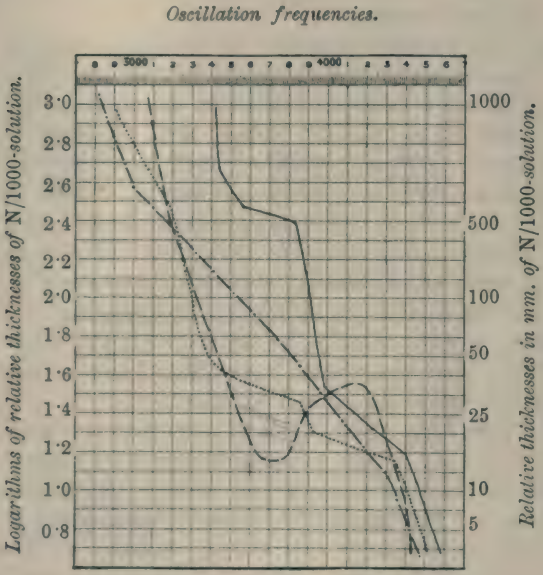
* The vapour spectra were observed in a 200 mm. tube 21 mm. in diameter, the light of the cadmium spark being used. The tube was placed in an air-bath heated to the required temperature and maintained at this temperature for some time. Excess of the substance was used, and before taking a photograph the tube was opened to the air for an instant by means of a tap. Temperatures up to 150° were reached in this way.

(T., 1912, **101**, 1520, etc.). λ 2791 w., 2785 w., 2770 to 2766 w. band, 2756 to 2749 str. band, 2715 str., 2703 to 2694 str. band, 2689 to 2678 str. band, 2658 f.str., 2649 f.str., 2637 f.str., 2632 to 2628 str. band, 2626 to 2616 str. band, 2615 to 2610 str. band, 2604 w., 2602 w., 2593 w., 2581 w., 2531 f.str., 2520 w.; the rays are then transmitted to λ 2220.

Most of the wider bands are really the effect of a number of very weak, sharp bands, which almost run together into one wider band. At higher temperatures this coalescence is more complete, and at 50° two of these bands are distinct, and have their heads at λ 3610 and λ 3760. It is noteworthy that this is nearly the position occupied by the two solution bands of anisole (Baly and Ewbank, *loc. cit.*), and is almost identical with that of the bands of anisole vapour (Purvis and McCleland, T., 1912, **101**, 1520).



Full curve : *Phenyl mercaptan in alcohol.*
Dash curve : *Phenyl mercaptan with sodium ethoxide.*
Dotted curve : *Diphenyl sulphide in alcohol.*
Dot and dash curve : *Diphenyl disulphide in alcohol.*

Two narrow bands at λ 2835 and λ 2815 appear at 61° to 105°, and two more at λ 2867 and λ 2854 at 115° to 129°. At 105° almost all the sharp, narrow bands have coalesced to form one wide band from λ 2820 and λ 2430, which is almost identical in position with the single solution band of phenol.

The main feature of the vapour spectrum of phenyl mercaptan is the strong general absorption. At 43° and 763 mm. pressure, two weak bands occur, extending from λ 2870 to λ 2859, and from λ 2798 to λ 2778 the rays being transmitted as far as λ 2600. The position of these bands is in approximately the same position as the first extension of the spectrum of the alcoholic solution of this substance.

The spectrum of diphenyl ether vapour at 81° and 761 mm. pressure showed two weak bands, which were most marked at 122°, at which temperature they extended from λ 2798 to λ 2768, and from λ 2710 to λ 2690. At 133° there was one band from λ 2798 to λ 2590. In this case, also, the vapour and solution bands are in almost the same position.

Although the solution spectrum of diphenyl sulphide contains no bands, the vapour of this substance at 764 mm. showed a large number, which were most numerous at 46° and persisted to 76°. Amongst these bands the following were marked: λ 2715 w., 2706 w., 2695 w., 2691 str., 2685 w., 2679 str., 2659 w., 2655 str., 2643 w., 2633 w., 2622 str., 2611 w., 2609 w., 2604 w., 2600 w., 2596 w., 2591 w., 2587 w.; general absorption begins at λ 2440. At 135° only general absorption from λ 2860 was observed. The vapour spectrum of diphenyl sulphide is therefore a banded spectrum, and there is some indication of grouping of the narrow bands between λ 2695—λ 2679, λ 2655—λ 2611, and λ 2609—λ 2591. These positions correspond with the middle portions and points of inflexion of the spectrum of the solution.

In all the foregoing examples it is seen that the position of the bands of the spectra of the vapours corresponds with the position of the bands in the alcoholic solution or with the extensions of the solution spectra. The spectra of diphenyl sulphide are, from this point of view, particularly interesting, because in this case we have the extensions in the spectrum definitely associated with bands in the vapour spectrum. These extensions of the spectrum may therefore be considered as bands of extremely small persistency. The marked effect of the thiol group in suppressing the characteristic bands of benzene is similar to that of certain other substituents, which are assumed to possess "residual affinity," such as iodine and the nitro-group. A solution of iodobenzene gives no bands, and the single band of nitrobenzene is of very slight persistency.

We desire to express our thanks to the Research Fund Committee of the East London College for a grant towards the cost of this investigation.

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